UNIVERSITY *of* DELAWARE

NC STATE UNIVERSITY

MULTIFUNCTIONAL FLEXIBLE COMPOSITES BASED ON CONTINUOUS CARBON NANOTUBE FIBER

Tsu-Wei Chou (PI)

Yuntian T. Zhu (Co-PI)

Annual Grantees'/Contractors' Meeting on
Mechanics of Multifunctional Materials & Microsystems

Arlington, VA • August 2, 2012

OUTLINE

- Introduction
- Carbon Nanotube Fibers
  - Experimental Characterization
  - Theoretical Analysis
- Carbon Nanotube Composite Fiber
  - Interfacial Shear Strength Measurements
  - Infusion Characterization
  - Torsional Behavior
- Multi-functional Flexible Composites
- Road Map of Research Integration and Optimization

INTRODUCTION

Shortcomings in Current CNT Reinforced Composites

- Difficulty in dispersing the highly agglomerated CNTs
- Lack of control of CNT orientation and distribution in the matrix material
- Morphologies of the reinforcement phase:
  low aspect ratio
  isotropic
  homogeneous

Chou *et al*., *Comp. Sci. Tech.* **(2010)**

INTRODUCTION

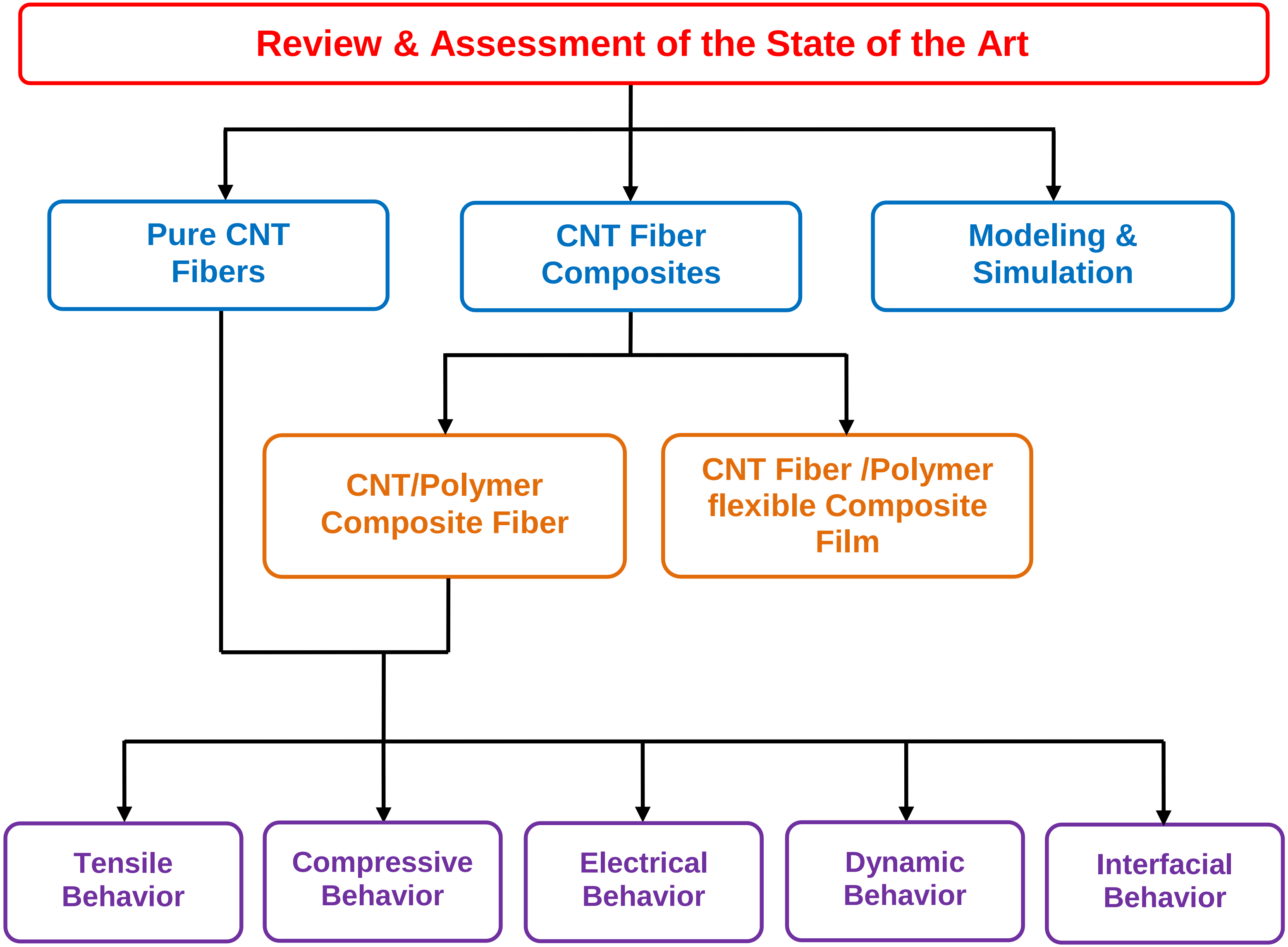
State of the Art

- Success in the development of long continuous CNT fibers in recent years at the Co-PI's laboratory and worldwide
- Attractive attributes of CNT-fibers: light weight, high conductivity, flexibility in deformation, large strain to failure
- Timing is right to take advantage of such development for a concerted effort in CNT-fiber based multifunctional composite material development

OBJECTIVE AND APPROACH

- **Establish the scientific foundation for lightweight, ultrathin, flexible composites for multifunctional structures.**
  - **Continuous filaments will be spun directly from an aerogel of SWCNTs and MWCNTs or a MWCNT array or forest.**
  - **Through highly integrated experimental and theoretical research, their performance maps in multi-functionality will be defined and verified within the system context of thin membranes.**
  - **This research will create new avenues for electrically-conductive, high performance materials.**

1st YEAR ACCOMPLISHMENTS



Review & Assessment of the State of the Art

Pure CNT Fibers

CNT Fiber Composites

Modeling & Simulation

CNT/Polymer Composite Fiber

CNT Fiber /Polymer flexible Composite Film

Tensile Behavior

Compressive Behavior

Electrical Behavior

Dynamic Behavior

Interfacial Behavior

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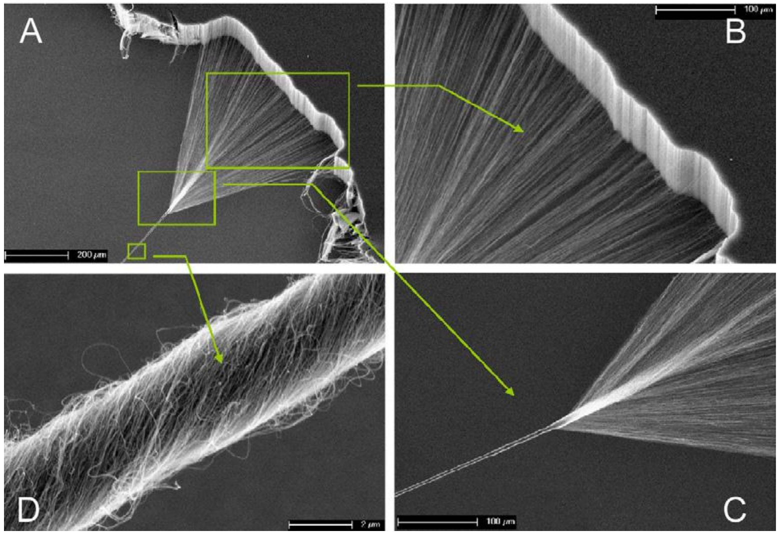
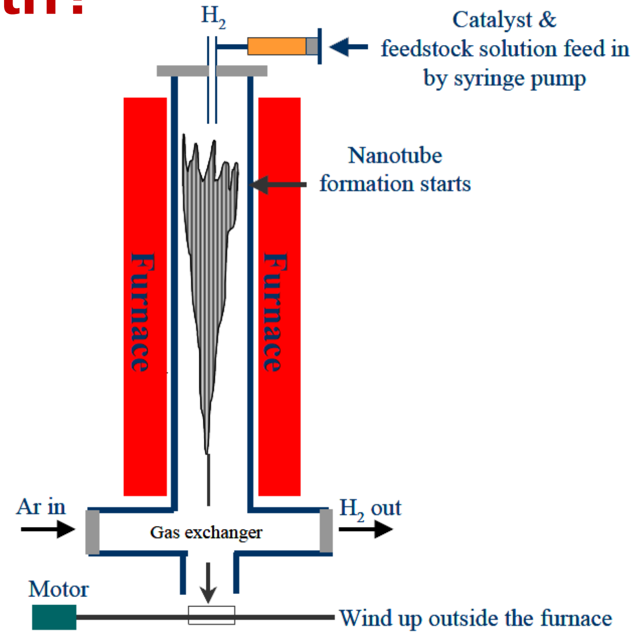
Fiber Microstructural Evolution

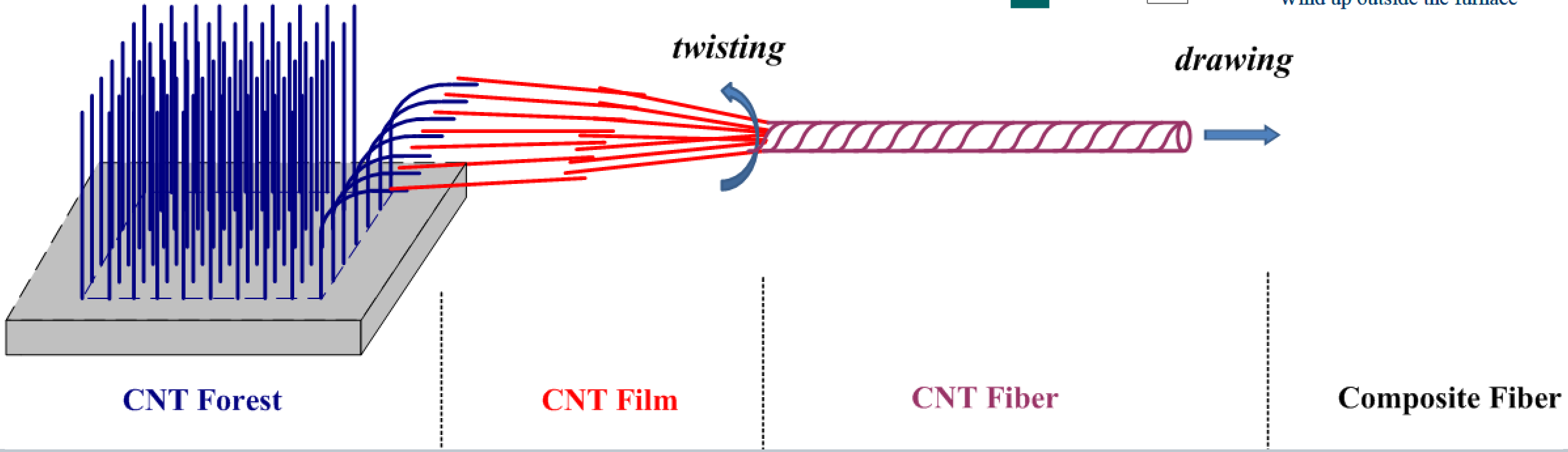
How do CNT fibers gain their strength?

dry spinning



aerogel spinning





MAJOR FACTORS CONTRIBUTING TO FIBER ELECTROMECHANICAL BEHAVIOR

CNT Forest ➔ CNT Film ➔ CNT fiber ➔ Composite fiber

- Forest height
- CNT type
  - -- SW, FW, MW
- CNT diameter
- CNT modulus
- CNT strength

- Fiber diameter distribution
  - --Tensile strength/modulus
- van der Waals interaction
- Twist angle, CNT distribution
- Intertube(bundle) compression
- Intertube(bundle) friction
- CNT entanglement, waviness
- Compressive/torsional behavior
- Piezoresistive behavior
- Dynamic response

- Fiber/polymer interphase
- Stress relaxation

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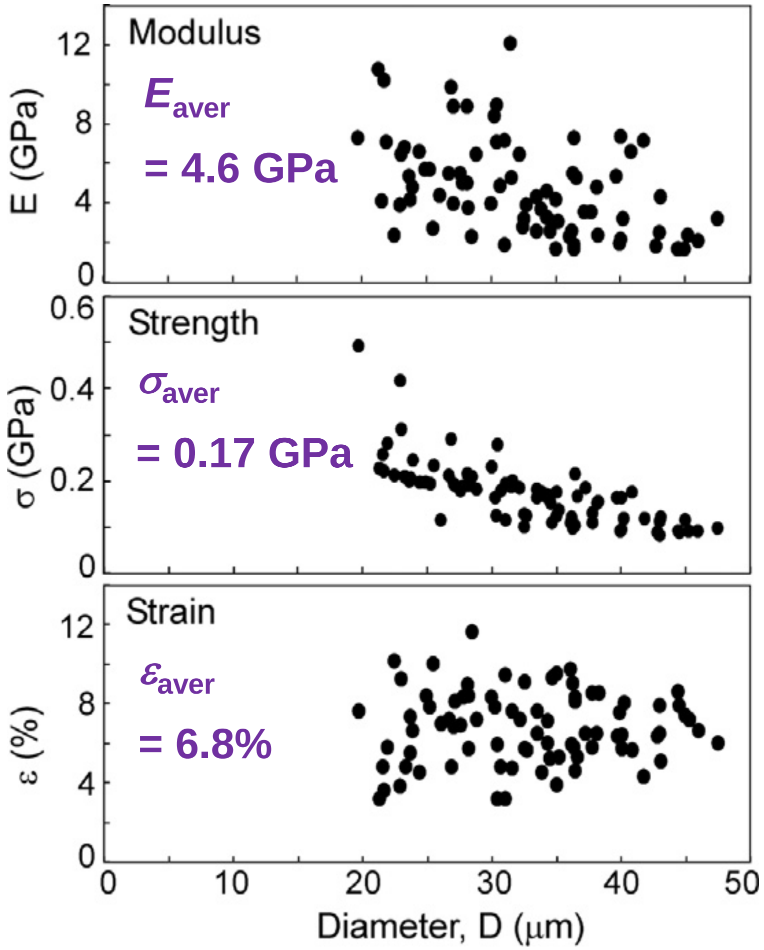
SINGLE CNT FIBER TEST

Statistical properties

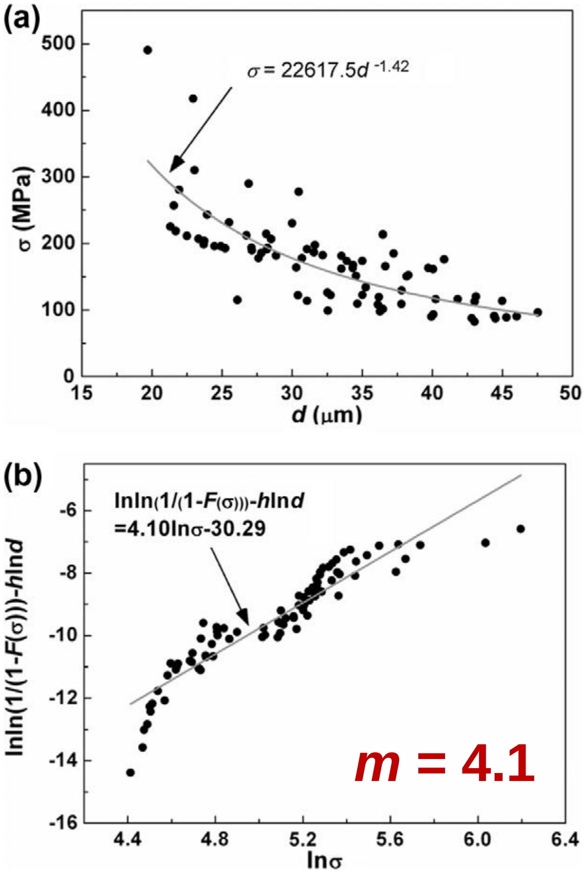
$$F(\sigma) = 1 - \exp\left[-d^h\left(\frac{\sigma}{\sigma_d}\right)^m\right] \qquad \sigma_d = \sigma_0 L^{-1/m}$$



E_{aver} = 4.6 GPa

σ_{aver} = 0.17 GPa

ε_{aver} = 6.8%



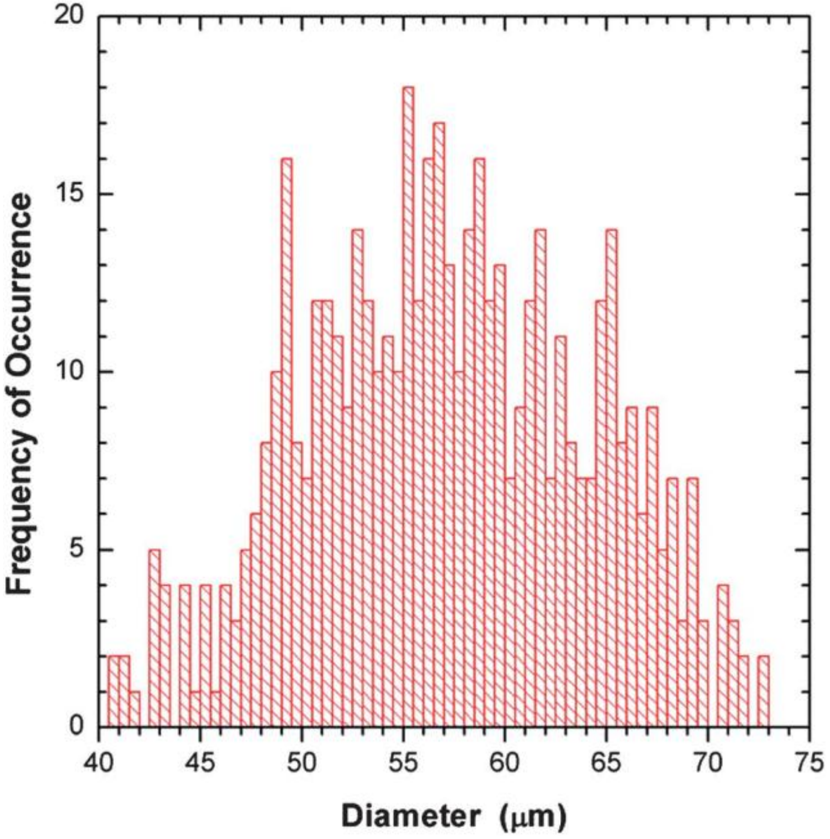
***m* = 4.1**

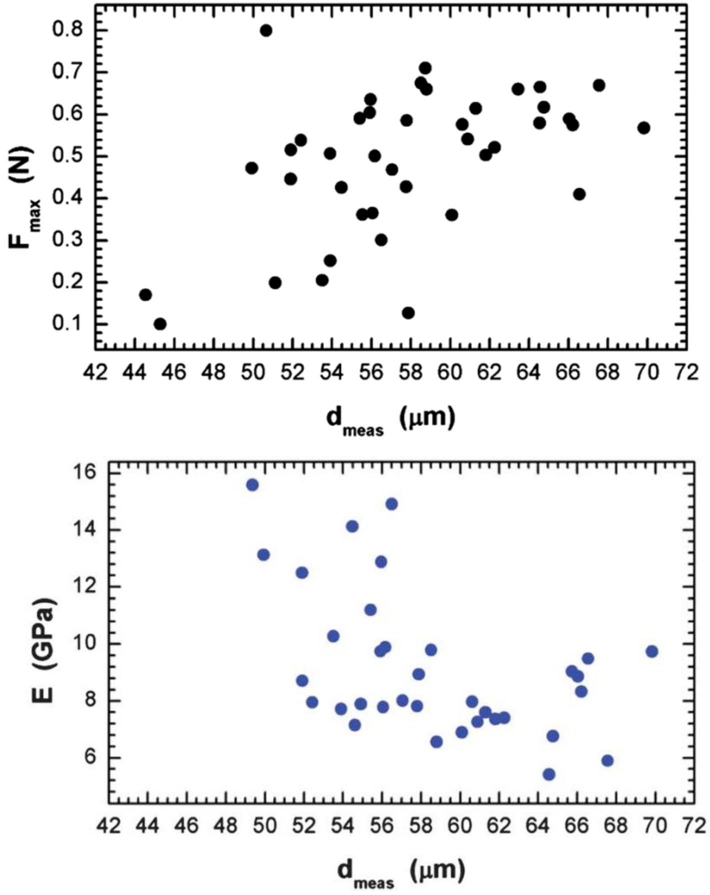
Weibull strength distribution

Deng , Zhu, Chou *et al.*, *Carbon* (2011)

SINGLE CNT FIBER TEST

- **Diameter Distribution along the fiber**



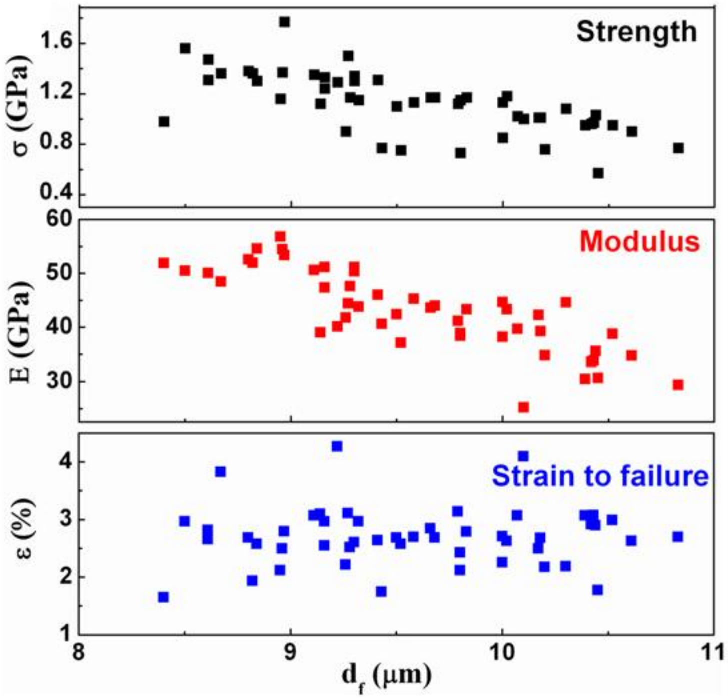


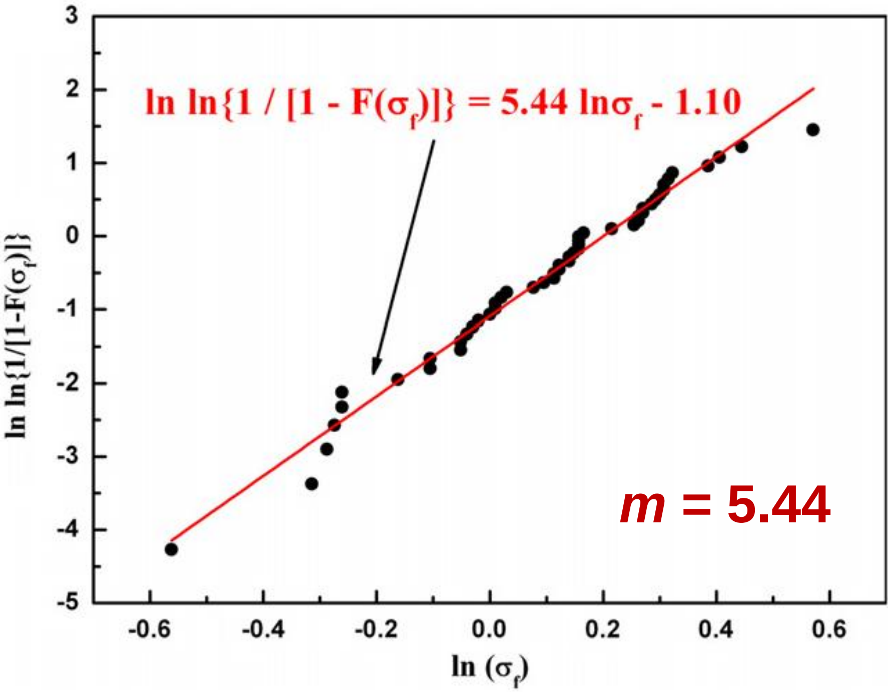
- **Peak force and modulus varies significantly with the fiber diameter**

Wu, Chou *et al.*, ***J. Mater. Chem.* (2012)**

SINGLE CNT FIBER TEST

Small diameter dispersion





m = 5.44

- ***Strength***: 1.2 ± 0.3 GPa
- ***Modulus***: 43.3 ± 7.4 GPa
- ***Failure strain***: 2.7 ± 0.5%

➢ ***Weibull strength distribution***

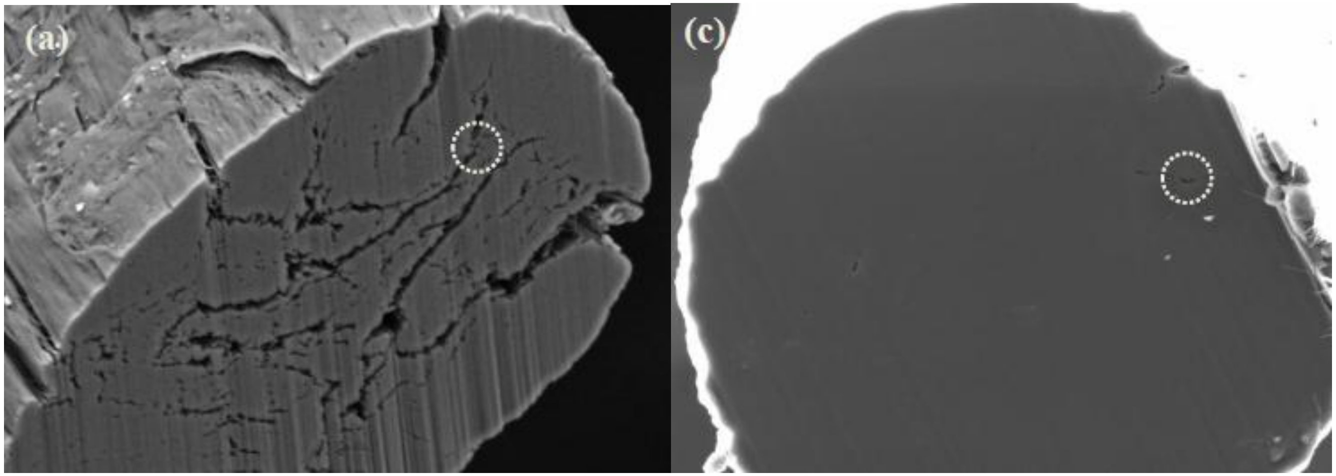
- **Less scattered than carbon and glass fibers**

Zu, Zhu, Chou *et al.*, *Carbon* **(2012)**

SINGLE CNT FIBER TEST

CNT/Epoxy Composite Fiber

- ***Epoxy infiltration*** **effectively enhances the strength and modulus of CNT fibers, but reduces the failure strain.**
  - ***Strength*****:** 1.4 Gpa → 1.77 GPa
  - ***Modulus*****:** 66 GPa → 93.4 GPa
  - ***Failure strain*****:** 2.54% → 1.99%

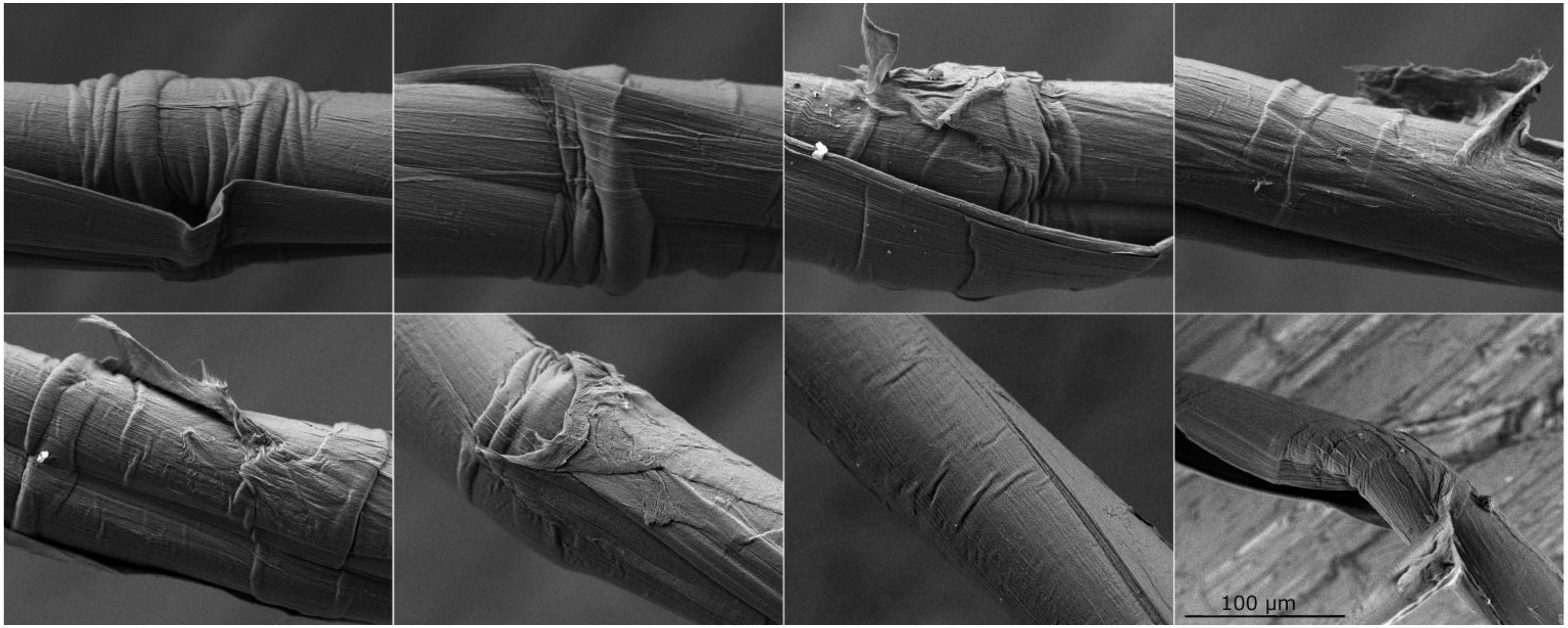


Cross section **of CNT fiber(left) and CNT/epoxy fiber(right)**

Zu , Zhu, Chou *et al*.**,** *ACS Nano* **(2012)**

TENSILE RECOIL TEST - PURE CNT FIBER

Under *highest* tensile recoil stress: kinking bands



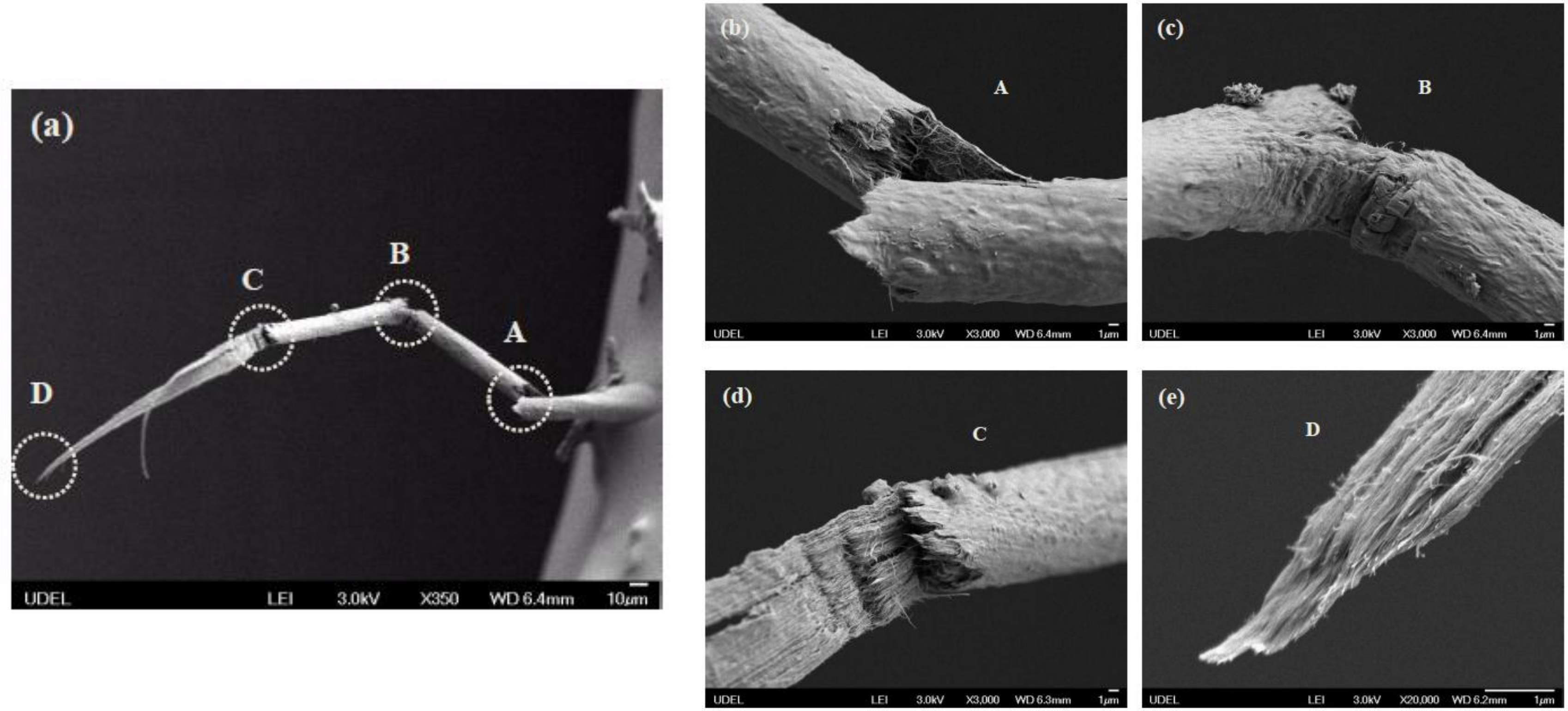
Compressive strength: ~172MPa

Wu, Chou *et al.*, *J. Mater. Chem. (2012)*

TENSILE RECOIL TEST – CNT/EPOXY FIBER

Under *highest* tensile recoil stress

- ***Compressive side***: severe kinking bands
- ***Tensile side***: brittle fractured

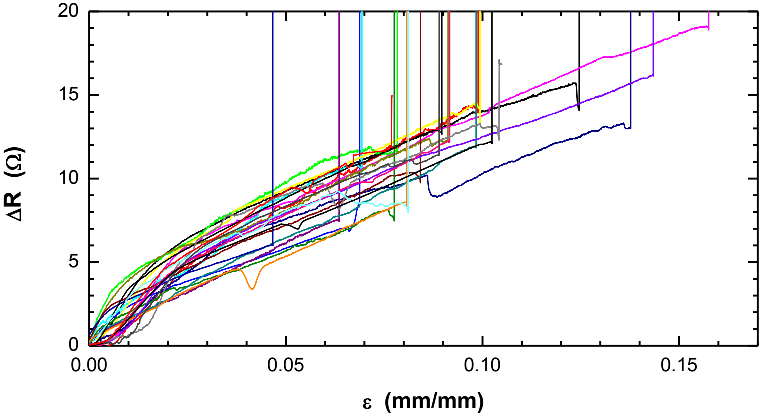


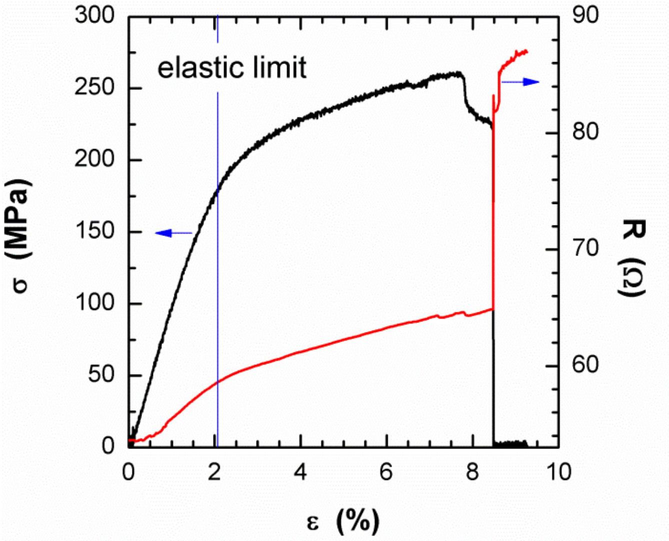
Compressive strength: ~573MPa

Zu , Zhu, Chou *et al.*, *ACS Nano* **(2012)**

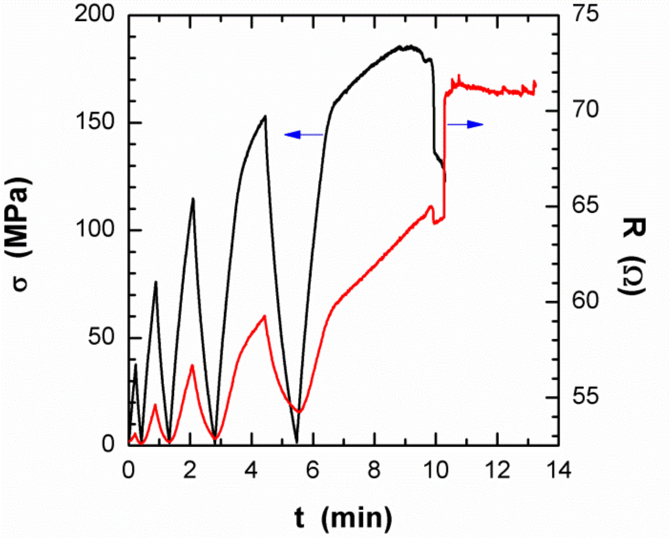
ELECTRICAL BEHAVIOR

- **Piezoresistive nature of the fibers**
  - ✧ **Potential for strain sensor application**





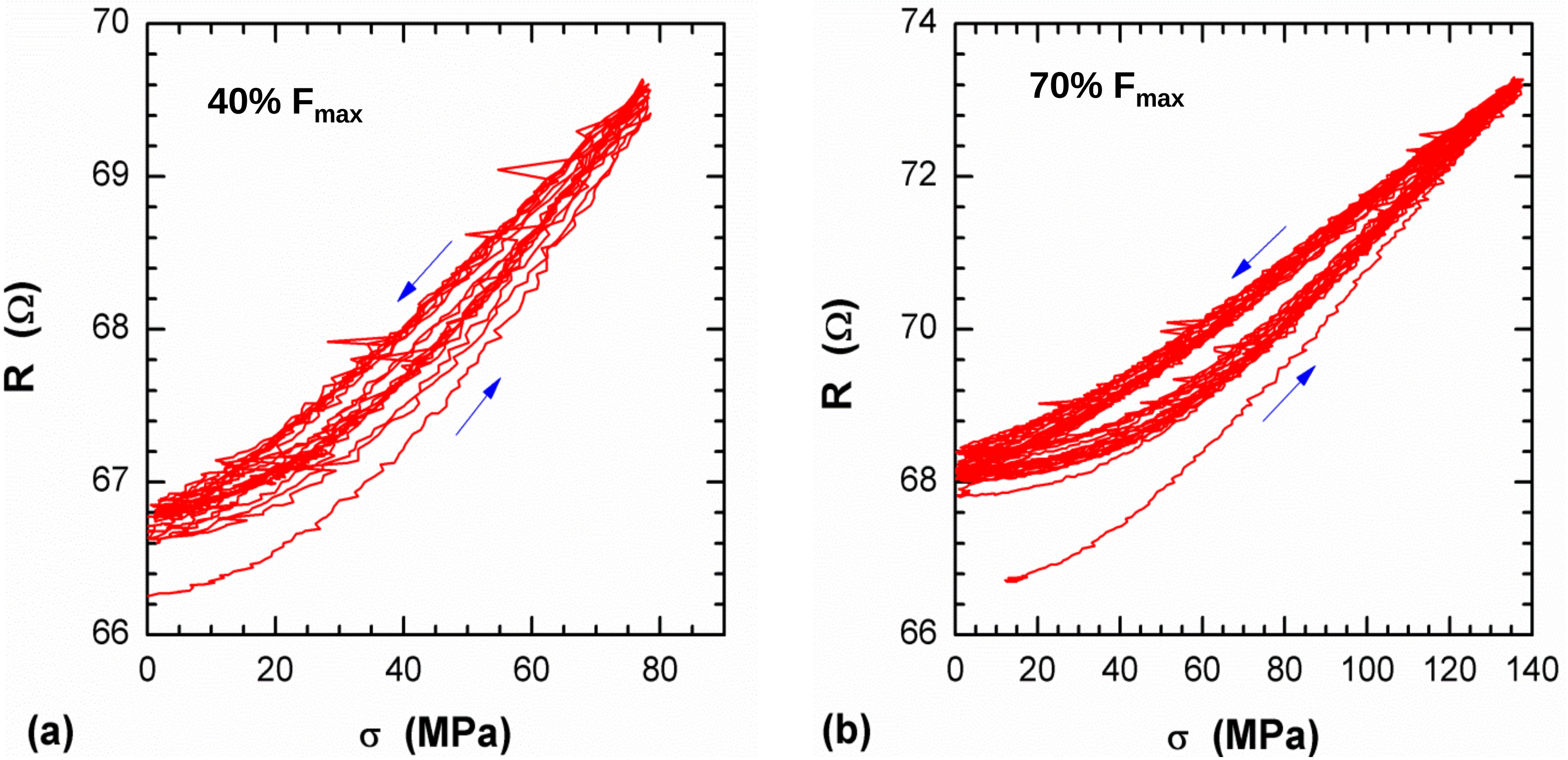
- **Both R and σ increase at different rates before and after the elastic limit of the fiber (top right).**
- **Cyclic experiments demonstrate that changes in electrical resistance are recoverable during the linear elastic regime (bottom right).**



Wu, Chou *et al.*, ***J. Mater. Chem.* *(2012)***

ELECTRICAL BEHAVIOR

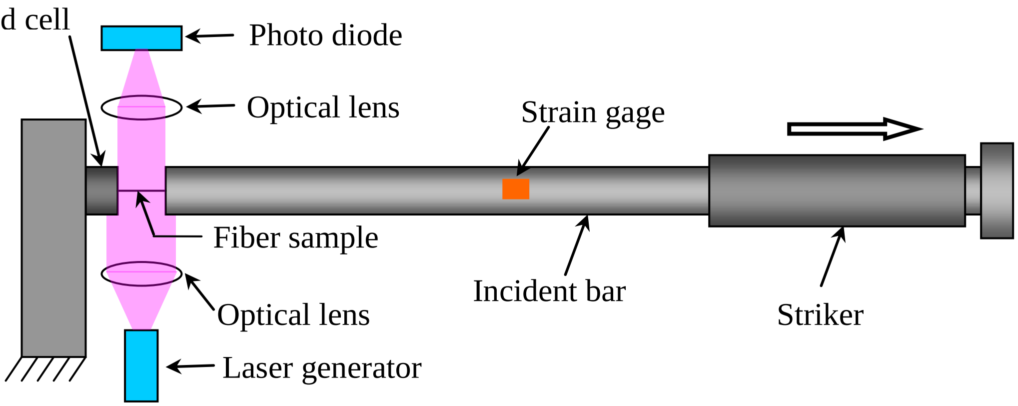
- **Electrical resistance hysteresis loops were observed under quasi-static cyclic tension loading**
  - **Possibly explanation: during unloading, twist and friction prevent immediate radial expansion of the fiber**

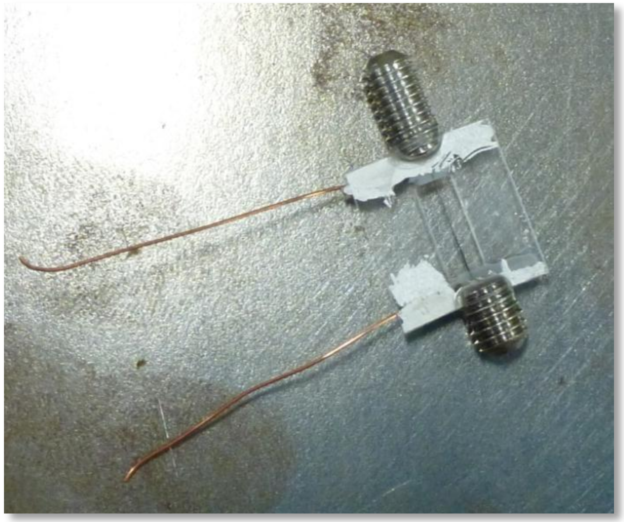


Wu, Chou *et al.*, ***J. Mater. Chem. (2012)***

DYNAMIC TESTS

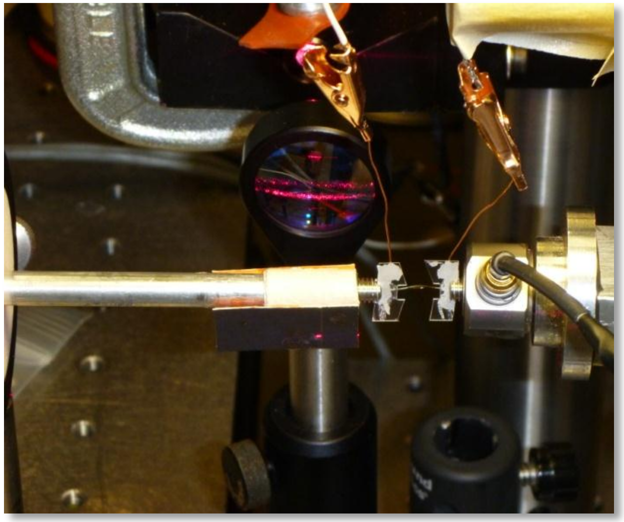
Dynamic tensile properties





Kolsky tension bar

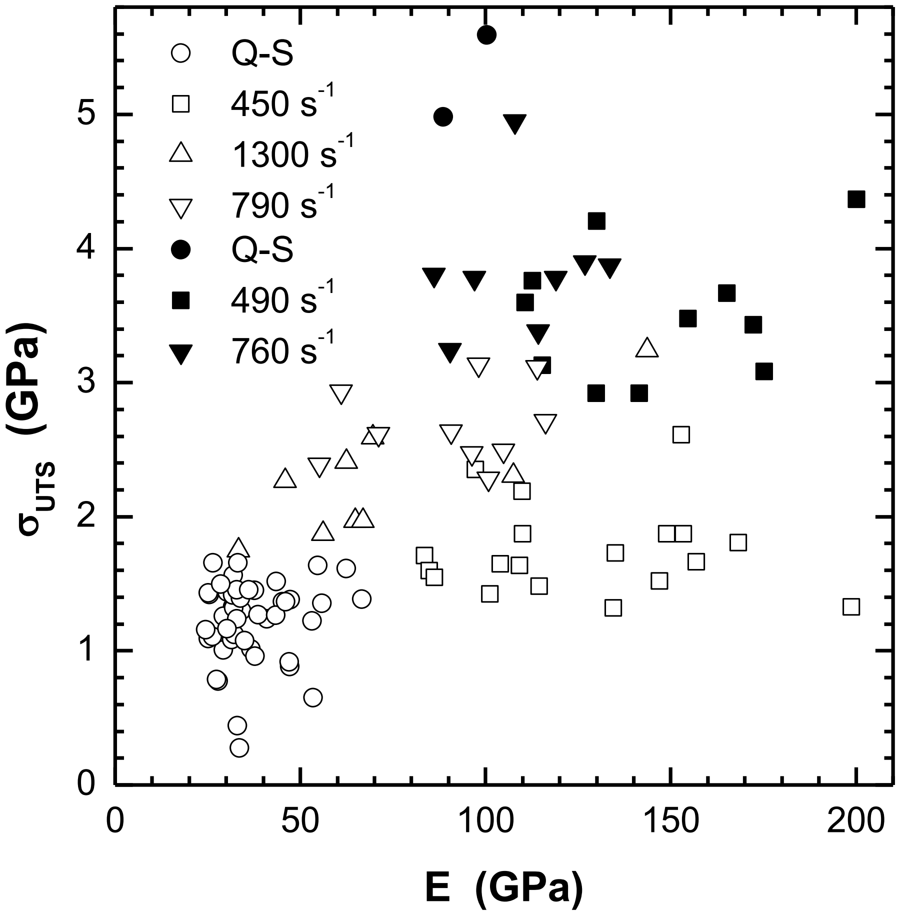
- **Fiber specimen attached using set screws**
- **Air driven striker bar – 25 and 50 psi**
- **22.24 N quartz–piezoelectric load cell**
- **Displacement measured via laser emitter-detector pair**



Wu, Nie, Hudspeth, Chen, Chou *et al*., *Carbon* (2012)

DYNAMIC ELECTROMECHANICAL BEHAVIOR

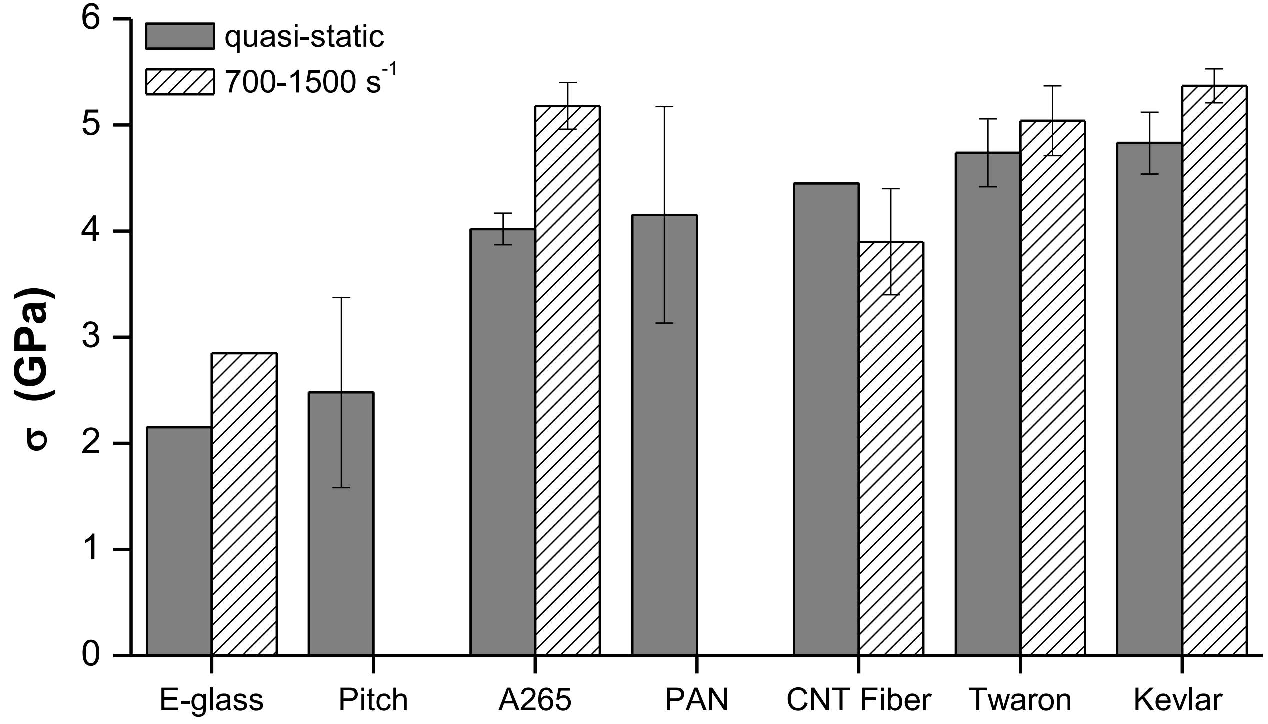
- **Quasi-static and dynamic behavior of as-spun carbon nanotube fiber (hollow) and chemically treated and stretched carbon nanotube fiber (filled).**



Wu, Nie, Hudspeth, Chen, Chou *et al*., *Carbon* (2012)

FIBER STRENGTH COMPARISON

- **After post-processing (chemical treatment and stretching), carbon nanotube fibers exhibit comparable properties to other high performance fibers.**



- **Significantly lower density**
- **1.4 g/cc vs. 1.8 g/cc (PAN)**

Wu, Nie, Hudspeth, Chen, Chou *et al*., *Carbon* (2012)
Lim *et al*., *Polymer Testing* (2010)
Lim *et al*., *Journal of Materials Science* (2010)
Wang and Xia, *Composites Science and Technology* (1997)
Kelly and Zweben, *Comprehensive Composite Materials* (2000)

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  - Near Term Research Goals
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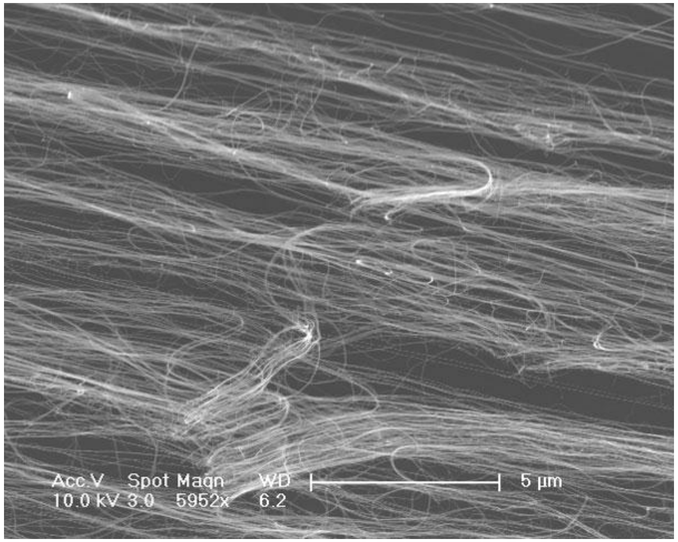
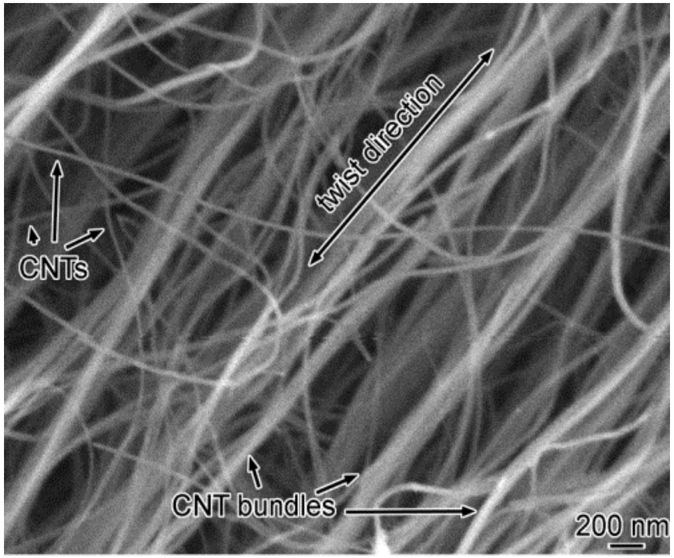
LOAD TRANSFER WITHIN A CNT FIBER

Load transfer mechanisms

- ♦ ***van der Waals force***
- ♦ ***Intertube/interbundle friction***
- ♦ ***CNT entanglements***

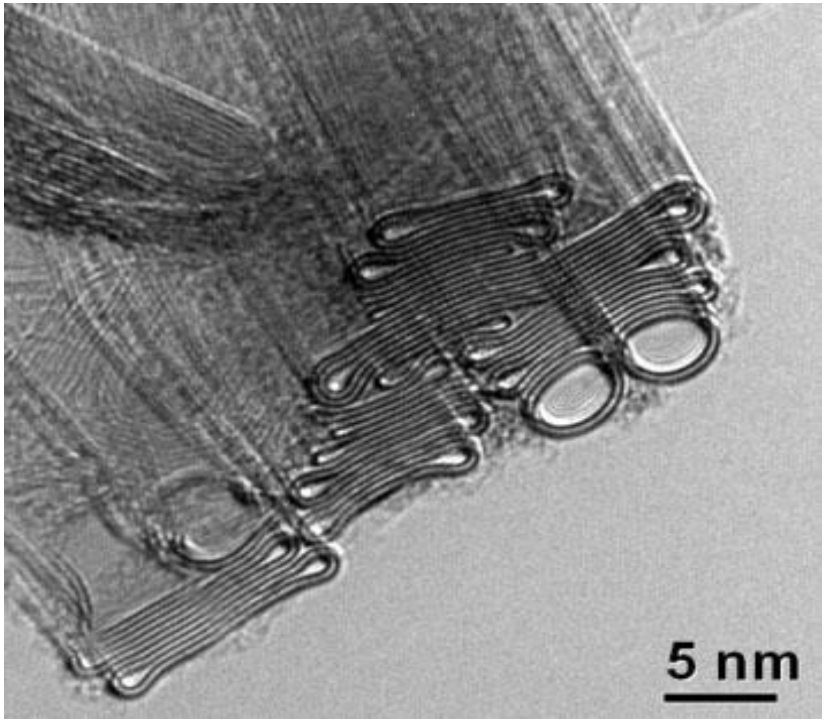




Zhang *et al*., *Adv. Mater.* **(2006);Deng , Zhu, Chou et al,** *Carbon* **(2011);**
***Lu* and *Chou*,** *J. Mech. Phys. Solids* **(2011)**

RADIAL DEFORMATION OF CNTS WITHIN A FIBER

Experimental observation



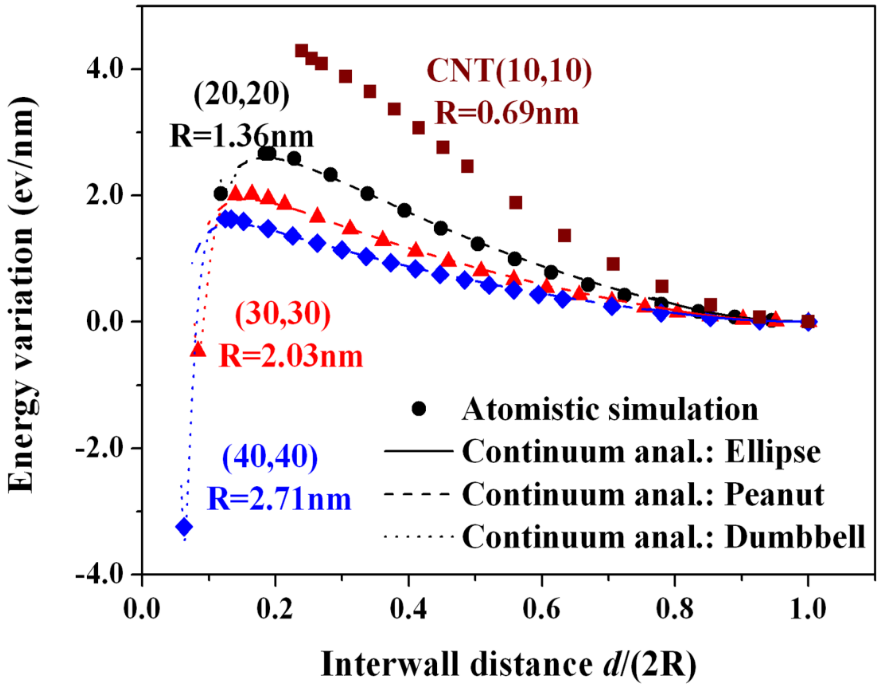
Benefits of radial collapse:

- **Increasing intertube contact area;**
- **Decreasing fiber cross sectional area**

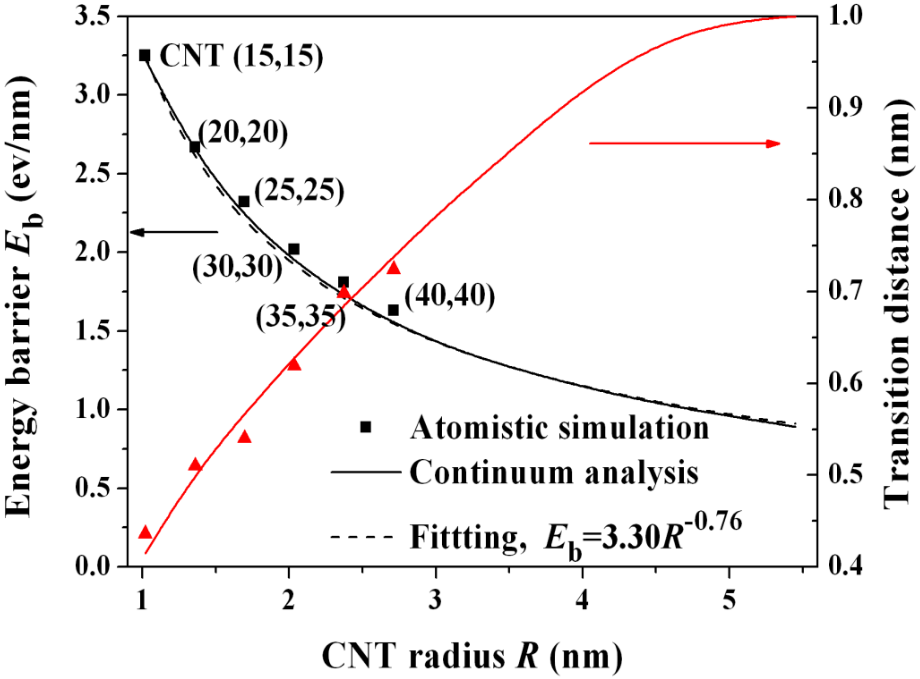
Motta *et al*., *Adv. Mater.* **(2007); *Zhang and Li et al***, *ASC Nano* **(2010)**

COLLAPSE OF CNTs WITHIN A FIBER

Energy variations



Energy barrier



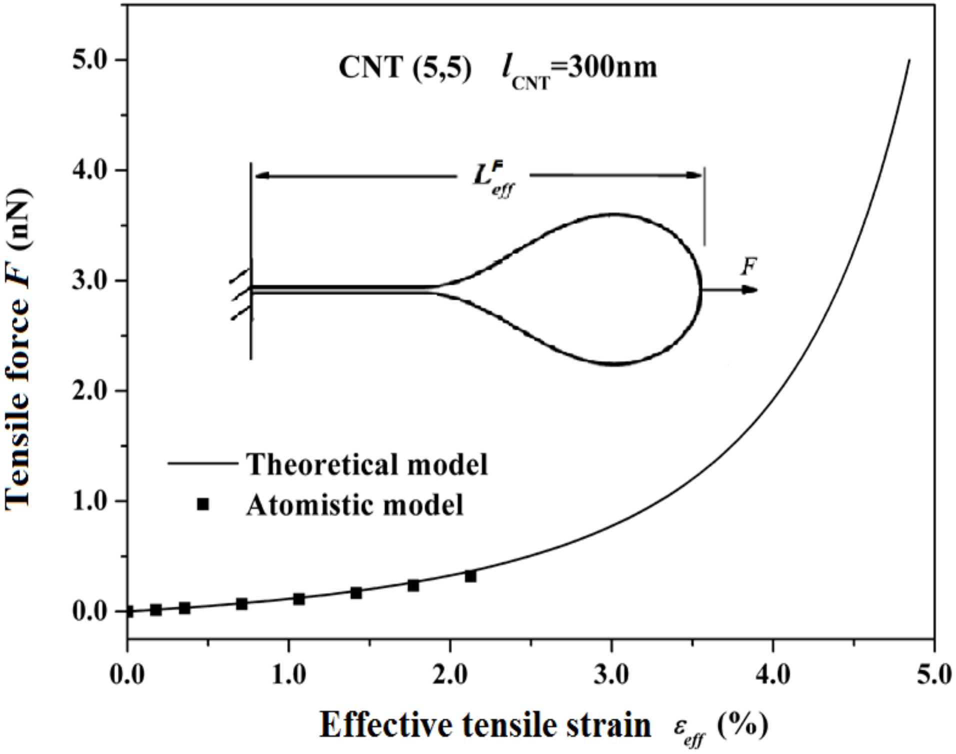
***R<1.05nm*: circular state is most stable**

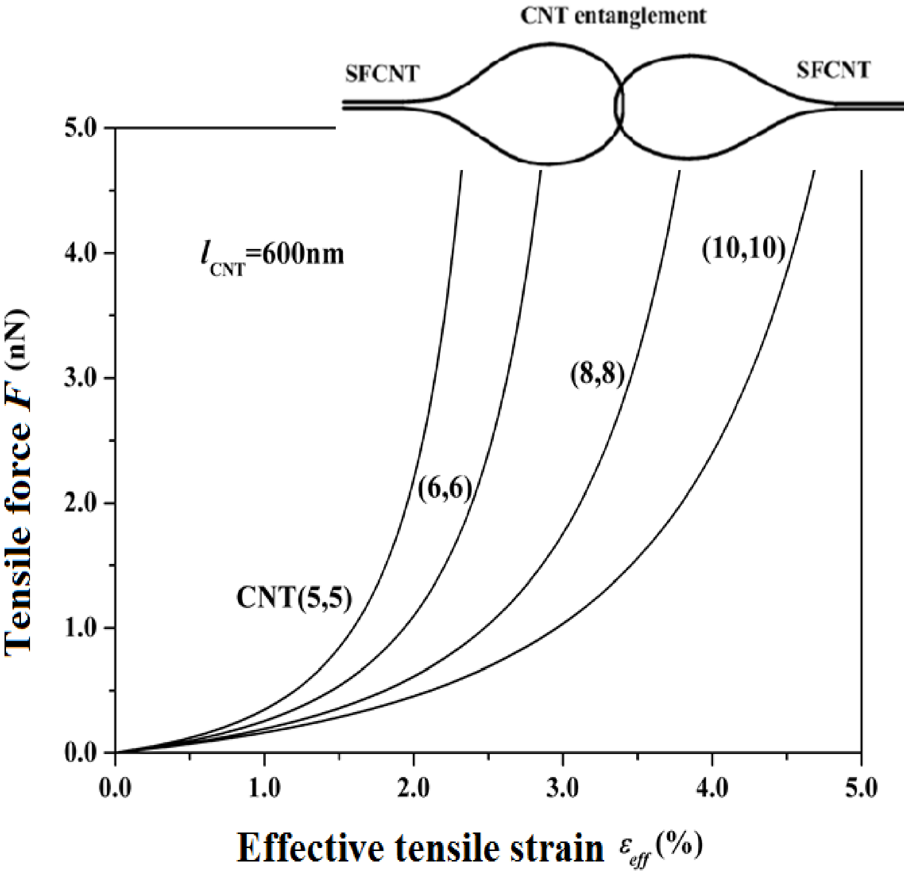
***1.05nm<R<1.90nm*: collapse state is metastable**

***R>1.90nm*: collapse state is most stable**

Lu, Chou and Kim, *Phys. Rev. B* **(2011)**

TENSILE PROPERTIES OF ENTANGLEMENT





Tensile stiffness increases with strain

Tensile stiffness decreases with diameter

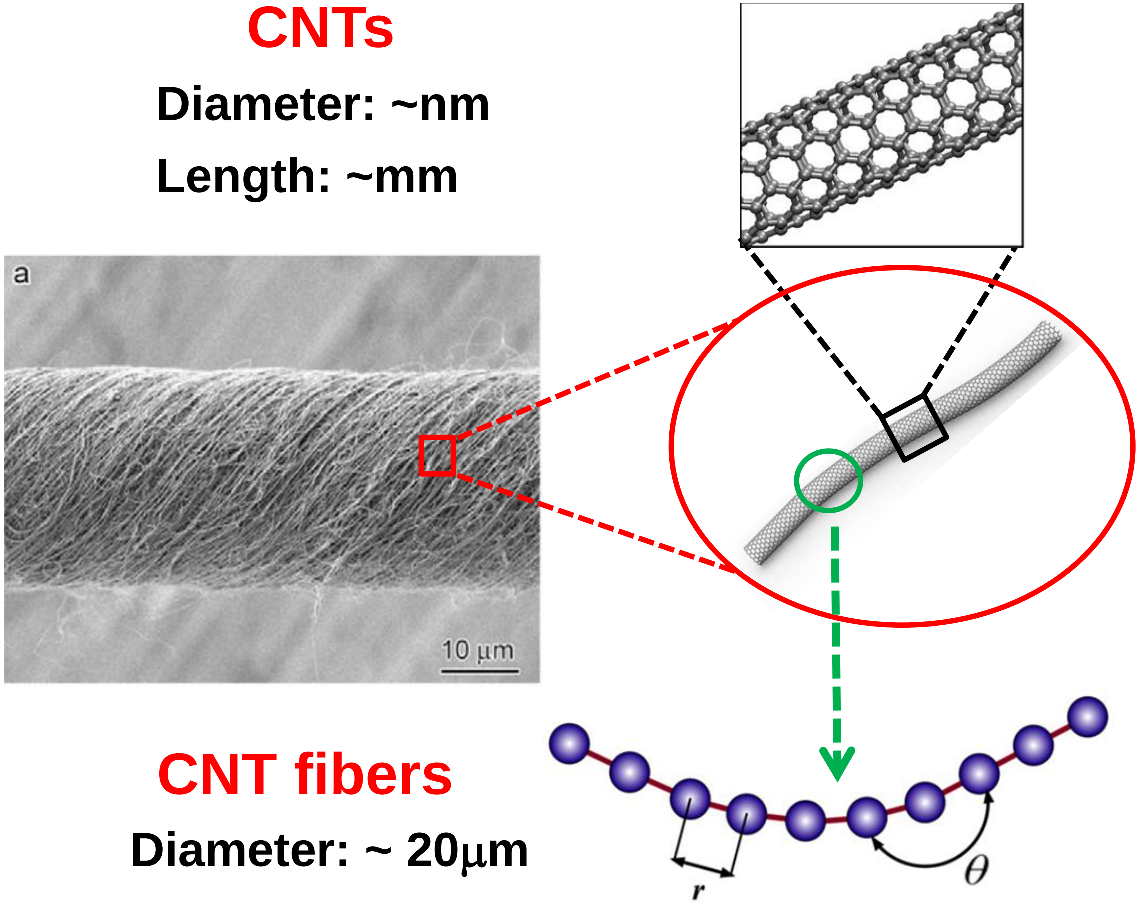
Lu and Chou, *J. Mech. Phys. Solids* **(2011)**

CNT FIBER SIMULATION

CNTs

Diameter: ~nm

Length: ~mm



All atomic MD Simulation

- **Node density: > 80/nm**

Coarse-grained MD Simulation

- **A line of beads connected by springs**
- **Node density : < 1/nm**

CNT fibers

Diameter: ~ 20μm

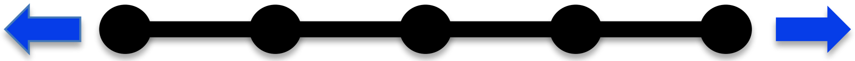
Length: ~ meters

Buehler , *J. Mater. Res*. (2006)**; Liu, Lu, Chou** *et al*. **(2012)**

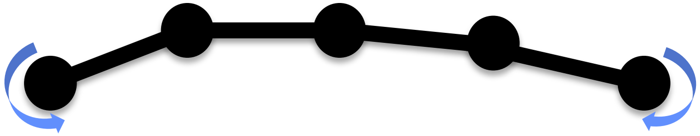
COARSE-GRAINED MOLECULAR DYNAMICS

Energy components

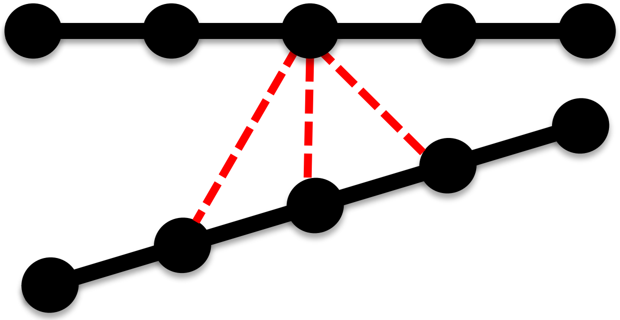
- *Bond Stretching Energy:* Elongation of springs



- *Bond Bending Energy:* Change of angles between neighboring springs



- *Pair interaction Energy*: Interaction between adjacent CNTs



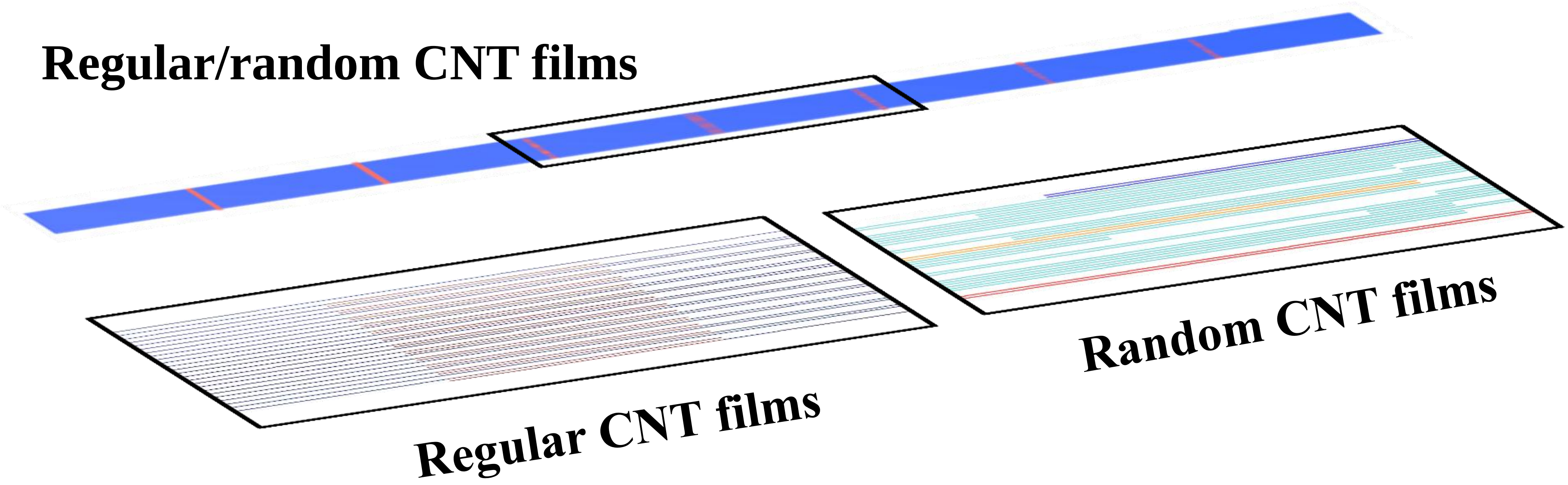
Total potential energy

$$E_{\text{total}} = \sum E_{\text{T}} + \sum E_{\text{B}} + \sum E_{\text{pair}}$$

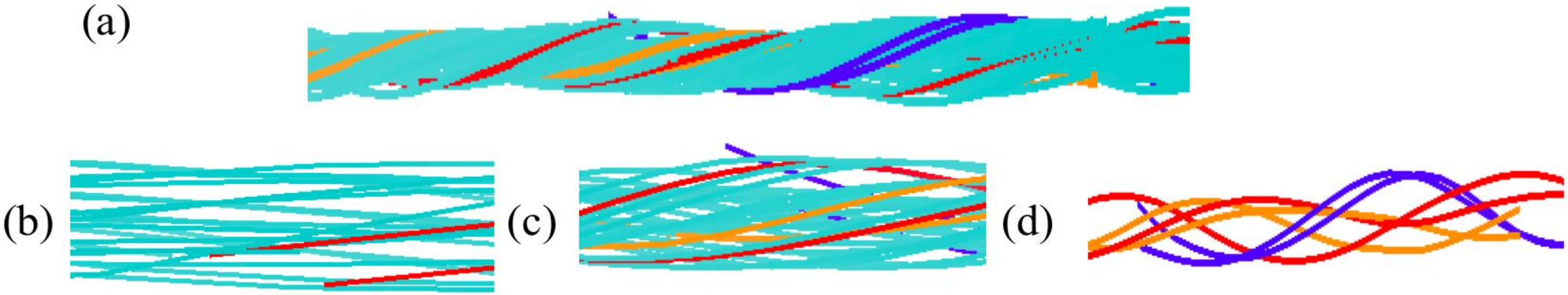
$$= \sum \frac{1}{2} k_{\text{T}} \left(r - r_0\right)^2 + \sum \frac{1}{2} k_{\text{B}} \left(\theta - \theta_0\right)^2 + \sum 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

FORMATION OF CNT FIBERS

Regular/random CNT films



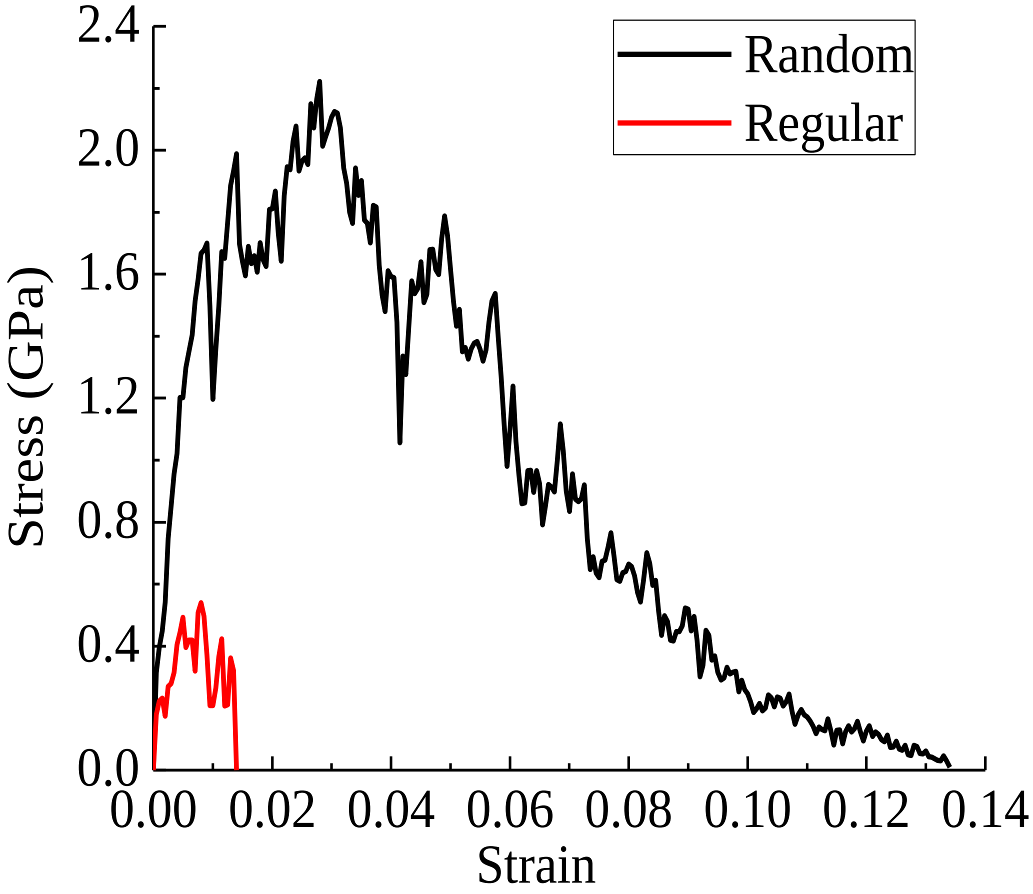
Twisted random CNT fiber



Liu, Lu, Chou *et al*. (2012)

EFFECT OF CNT DISTRIBUTION ON FIBER STRENGTH

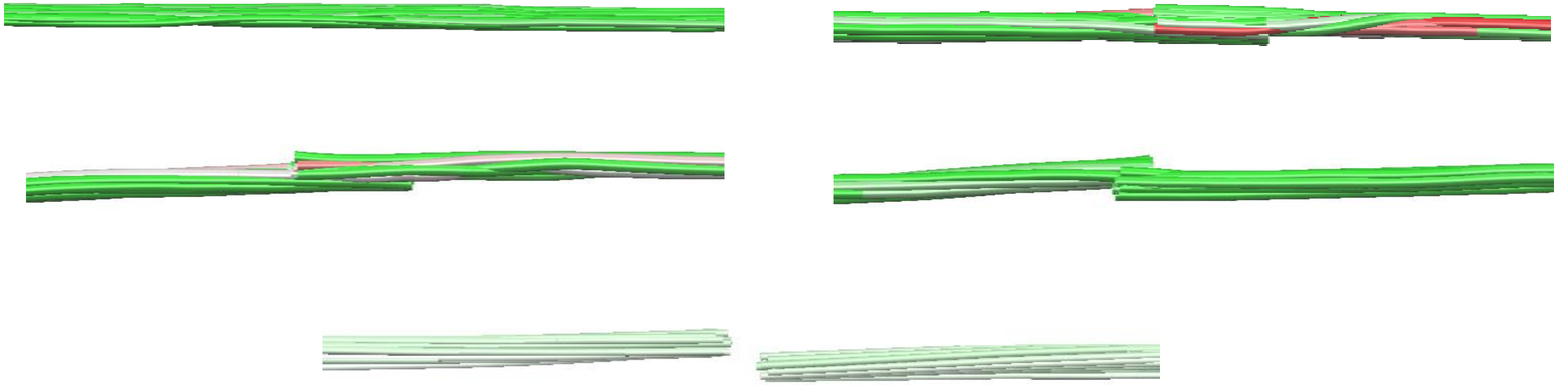
Stress-strain relations of twisted regular/random CNT fibers



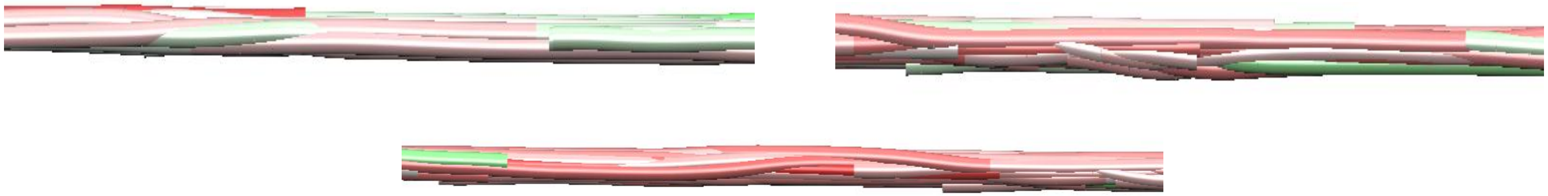
Liu, Lu, Chou *et al*. (2012)

CNT FIBER STRESS DISTRIBUTION UNDER TESNSION

- **Regular fiber**



- **Random fiber**



Liu, Lu, Chou *et al*. (2012)

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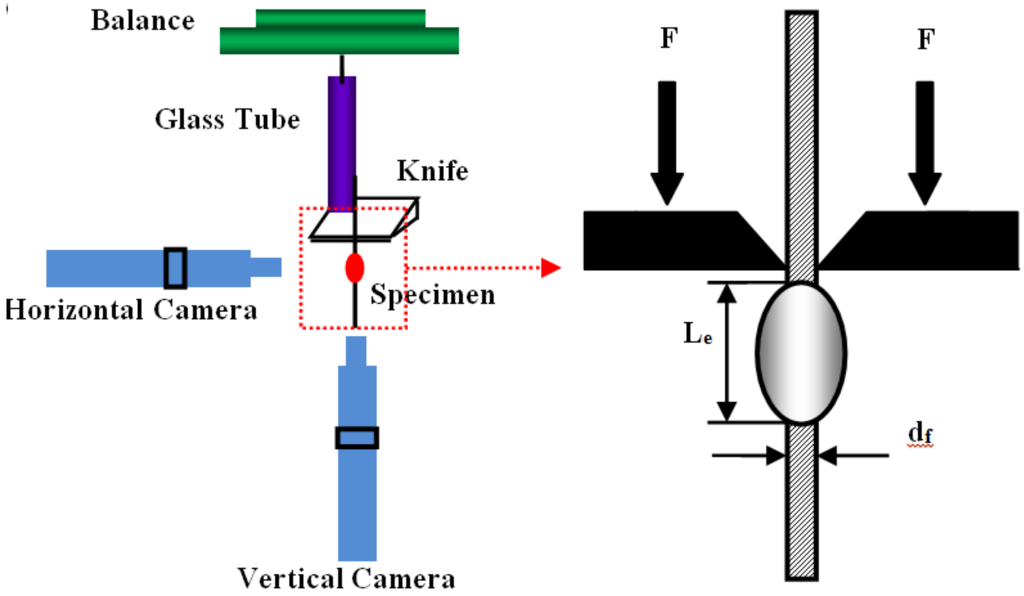
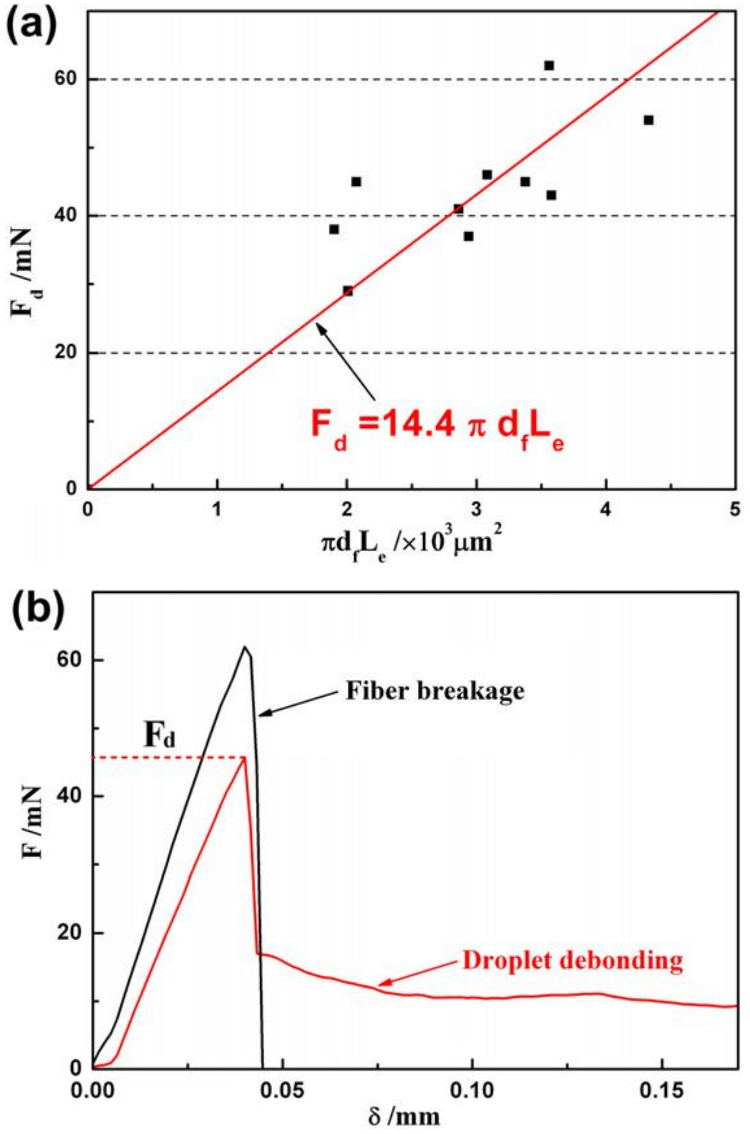
MICRODROPLET TEST



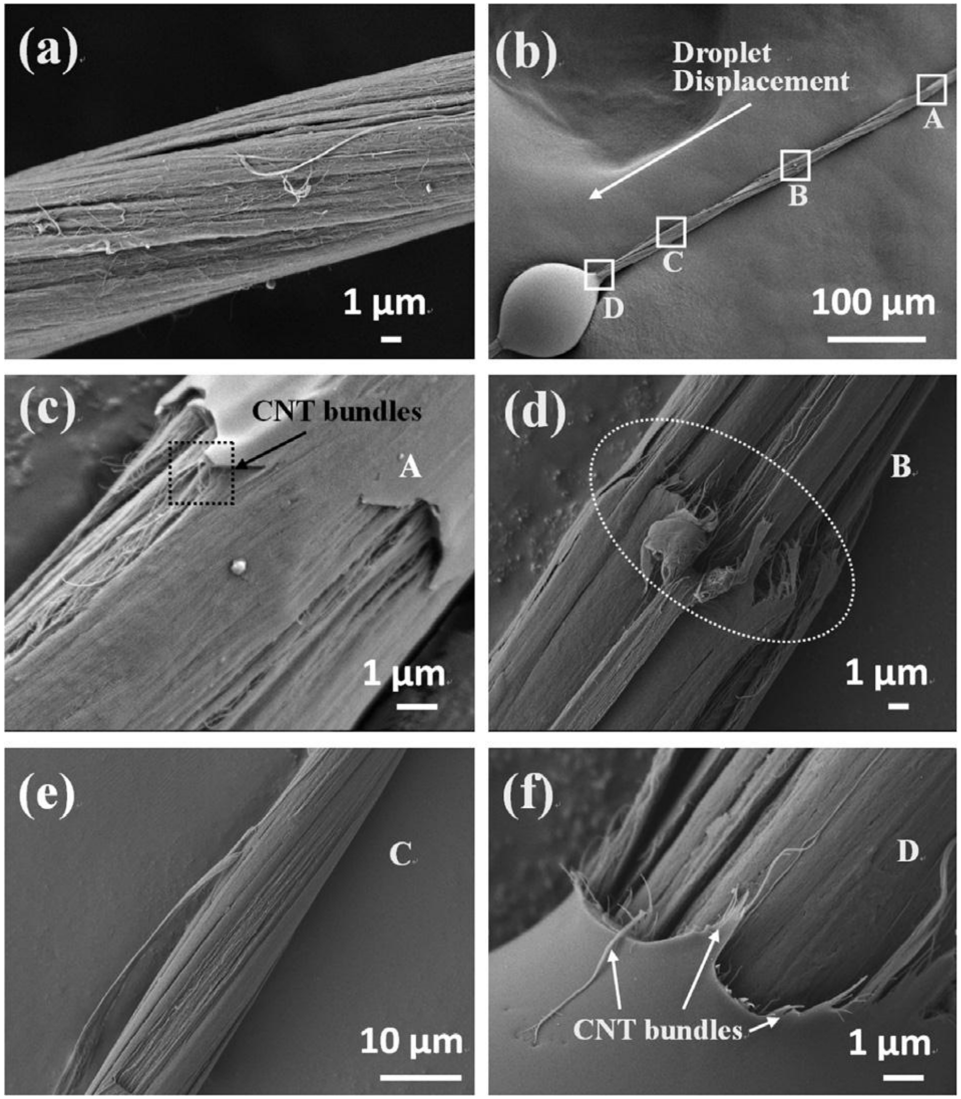


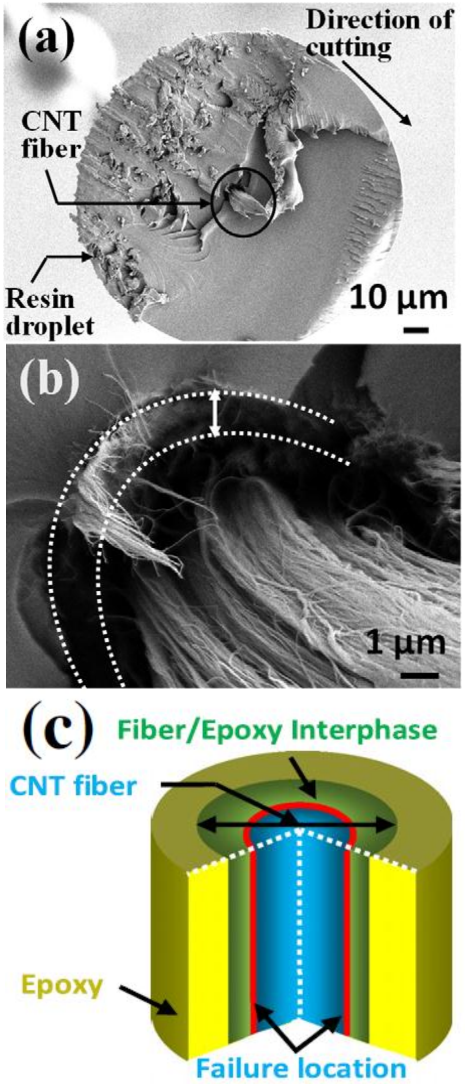
$$\text{IFSS} = \frac{F_d}{\pi d_f L_e} = \frac{\sigma_d d_f}{4L_e}$$

Effective Interfacial Shear Strength: 14.4 MPa

Zu, Zhu, Chou ***et al.*****,** ***Carbon*** **(2012)**

CNT FIBER/EPOXY INTERFACIAL DEBONDING





Zu, Zhu, Chou *et al.*, *Carbon* **(2012)**

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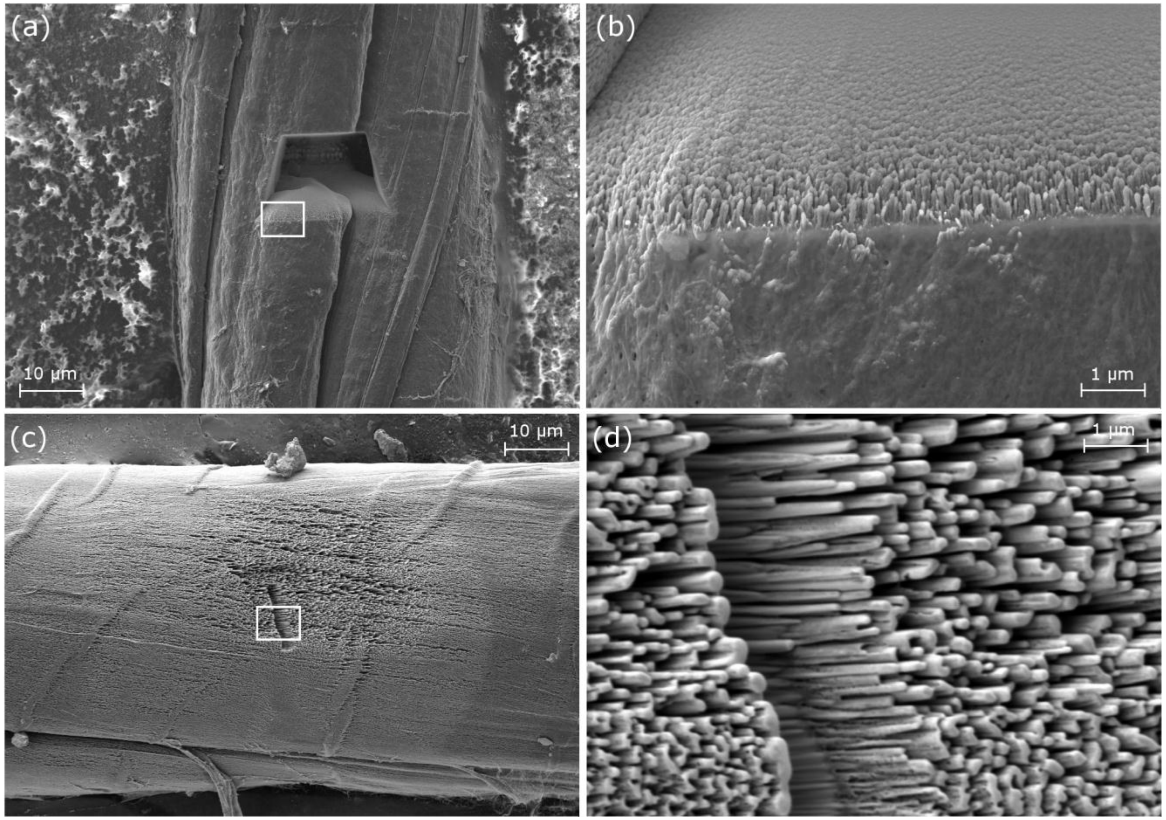
CNT FIBER INFUSION

- **Fibers are treated with nitric acid to promote adhesion with epoxy resin.**



  - **(a)-(b) infused fiber; (c)-(d) uninfused fiber**

Wu, Nie, Hudspeth, Chen, Chou, *et al*.**,** *Applied Physics Letters* **(2012)**

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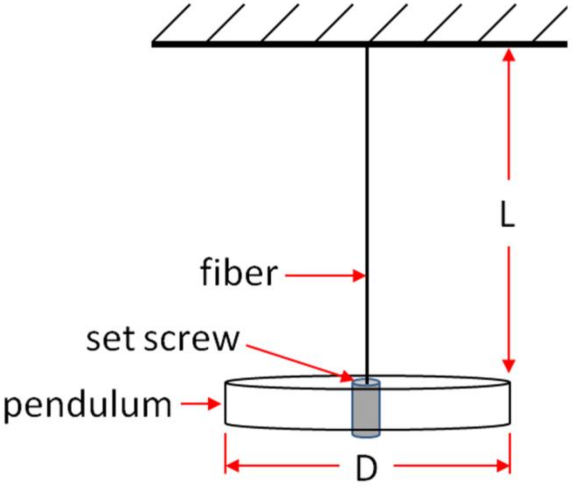
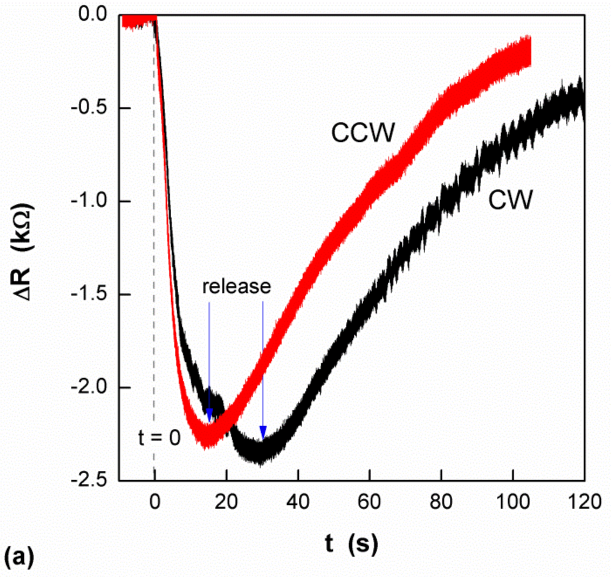
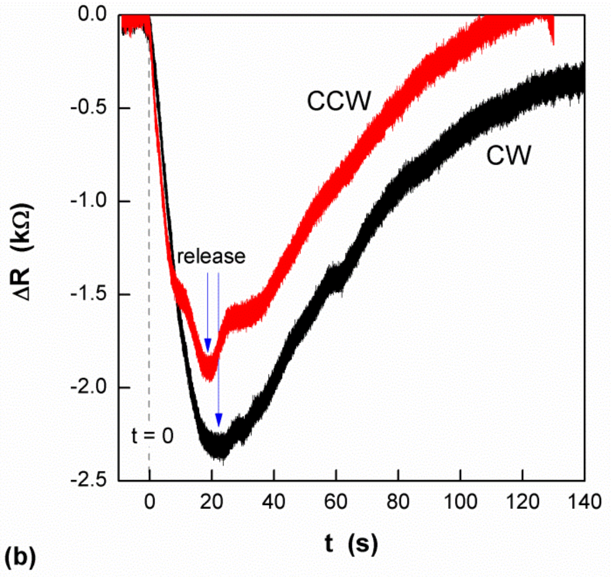
TORSIONAL BEHAVIOR

- **An average shear modulus of 0.40 ± 0.02 GPa for uninfused and 2.79 ± 0.64 GPa for infused fibers is measured.**







- **Both uninfused and infused fibers exhibit an electrical response to applied torsion demonstrating their ability to act as embedded torsional sensors.**

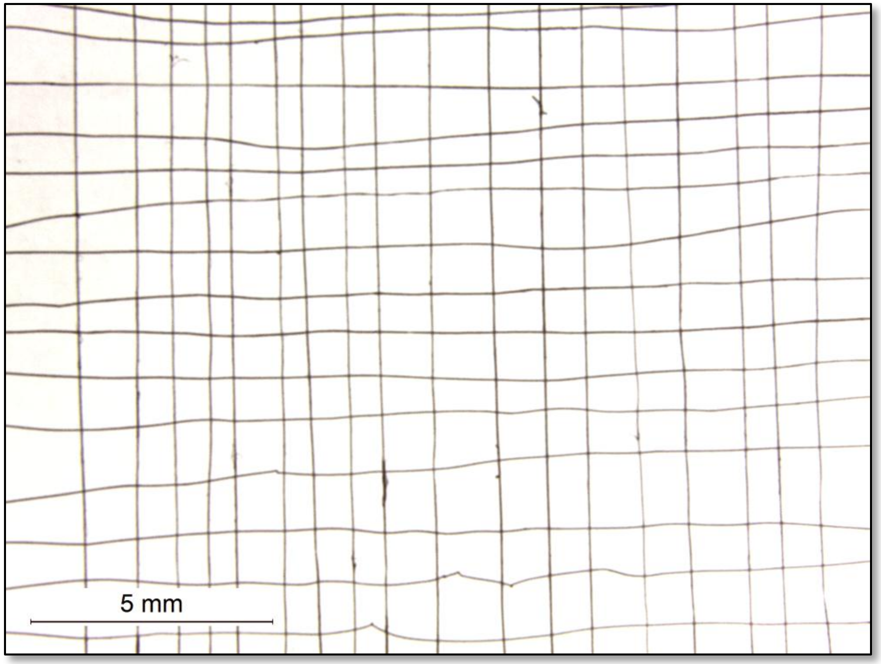
Wu, Nie, Hudspeth, Chen, Chou, *et al.*, *Applied Physics Letters* **(2012)**

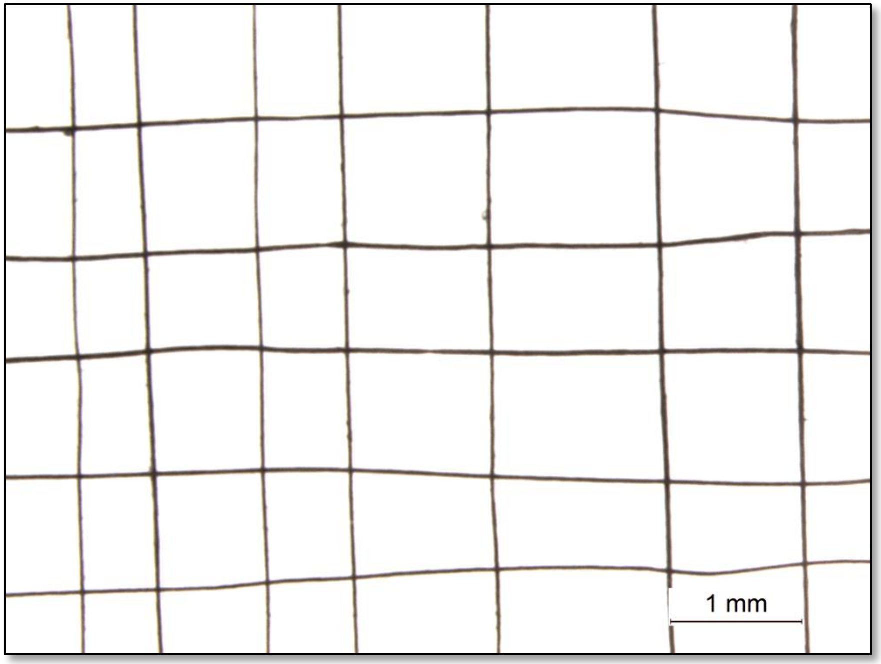
OUTLINE

- **Introduction**
- **Carbon Nanotube Fibers**
    - **Experimental Characterization**
    - **Theoretical Analysis**
- **Carbon Nanotube Composite Fiber**
    - **Interfacial Shear Strength Measurements**
    - **Infusion Characterization**
    - **Torsional Behavior**
- **Multi-functional Flexible Composites**
- **Road Map of Research Integration and Optimization**

WOVEN FABRIC PREFORMS

- **Current plain woven CNT fiber preforms, fabricated at NCSU, possess an average interfiber spacing of 1 mm.**





Multifunctional Flexible CNT Fiber Composites

Motivation

New Electronic Materials

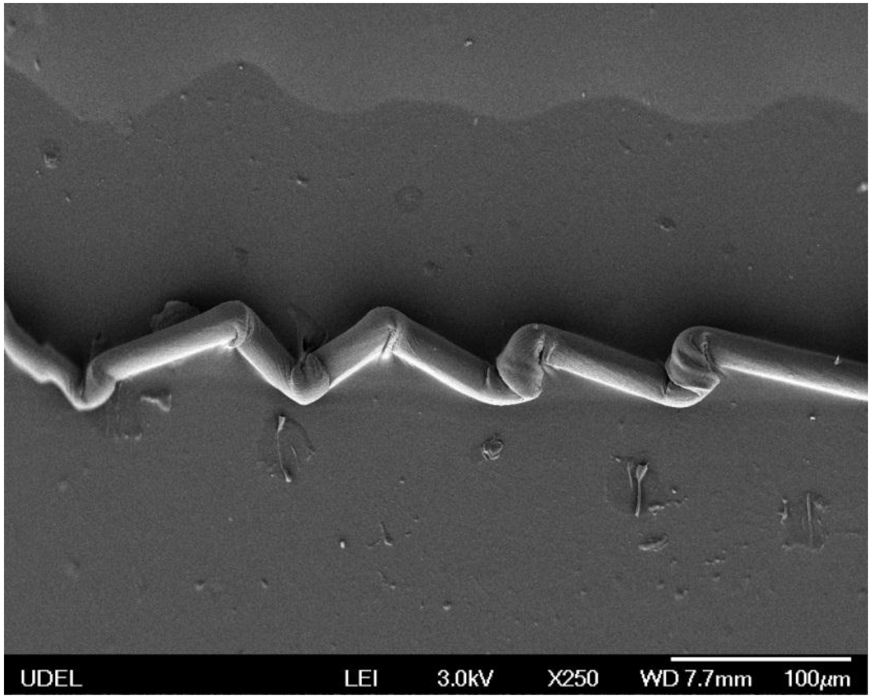
- **Bendable, stretchable, twistable, deformable**
- **Small resistance change**

CNT Fiber Characteristics

- **Electrical conductivity**
- **Flexibility**

Approach

- *Buckled CNT fiber / PDMS (polydimethylsiloxane) composites*



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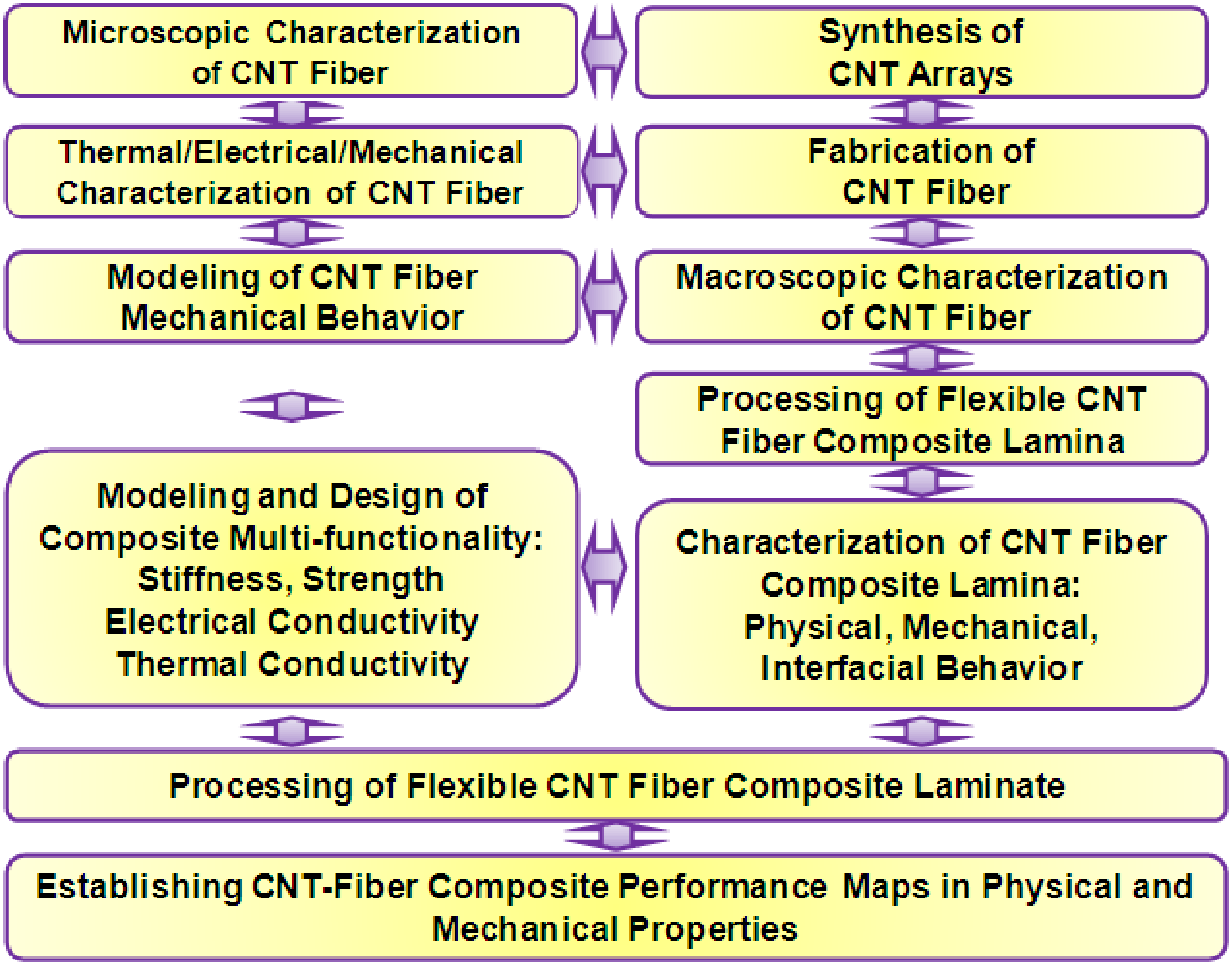
ROAD MAP OF RESEARCH INTERGRATION AND OPTIMIZATION



Microscopic Characterization of CNT Fiber

Thermal/Electrical/Mechanical Characterization of CNT Fiber

Modeling of CNT Fiber Mechanical Behavior

Modeling and Design of Composite Multi-functionality:
Stiffness, Strength
Electrical Conductivity
Thermal Conductivity

Synthesis of CNT Arrays

Fabrication of CNT Fiber

Macroscopic Characterization of CNT Fiber

Processing of Flexible CNT Fiber Composite Lamina

Characterization of CNT Fiber Composite Lamina:
Physical, Mechanical, Interfacial Behavior

Processing of Flexible CNT Fiber Composite Laminate

Establishing CNT-Fiber Composite Performance Maps in Physical and Mechanical Properties

PUBLICATION LIST

1. Zu M, Li QW, Zhu YT, Dey M, Wang GJ, Lu WB, Deitzel JM, Gillespie Jr. JW, Byun JH, Chou TW (2012) The effective interfacial shear strength of carbon nanotube fibers in an epoxy matrix characterized by a microdroplet test. *Carbon* 50:1271-1279
2. Wu AS, Chou TW, Gillespie Jr. JW, Lashmore D, Rioux J (2012) Electromechanical response and failure behavior of aerogel-spun carbon nanotube fibers under tensile loading. *Journal of Materials Chemistry* 22(14):6792-6798
3. Wu AS, Nie X, Chen WW, Chou TW, Lashmore D, Schauer M, Tolle E, Rioux J (2012) Carbon nanotube fibers as torsion sensors. *Applied Physics Letters* 100:201908
4. Wu AS, Nie X, Hudspeth MC, Chen WW, Chou TW, Lashmore D, Schauer M, Tolle E, Rioux J (2012) Strain rate-dependent tensile properties and dynamic electromechanical response of carbon nanotube fibers. *Carbon* 50(10):3876-3881
5. Lu WB, Zu M, Byun JH, Kim BS, Chou TW (2012) A State-of-Art Review of Carbon Nanotube Fibers: Oppertunities and Challenges. *Advanced Materials* 24:1805-1833
6. Zu M, Lu WB, Li QW and Zhu YT (2012) Characterization of carbon nanotube fiber compressive properties using tensile recoil measurement. *ACS Nano* 60:4288-4297
7. Zu M, Li QW, Zhu YT, Wang GJ, Byun JH, Chou TW (2012, submitted) Tensile stress relaxation: a critical issue of carbon nanotube-based fibers for load-bearing applications.
8. Wu AS, Chou T-W (July 2012, in press) Carbon nanotube fibers for advanced composites. *Materials Today*

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